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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

Express Mail Label No. EV334624913US

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Ofer	Sneh	Broomfield, Colorado

☐ Additional inventors are being named on the _____ separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

IMPROVED ALD APPARATUS AND METHOD

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ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification *Number of Pages*   65   ☐ CD(s), Number

☒ Drawing(s) *Number of Sheets*   21   ☒ Other (specify) Express Mail Certificate (1 page)

☒ Application Data Sheet. See 37 CFR 1.76 (3 pages)

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☒ Applicant claims small entity status. See 37 CFR 1.27.

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Respectfully submitted.   [Page 1 of 2]

SIGNATURE _____   Date   6/27/03

TYPED or PRINTED NAME   Phyllis K. Wood   REGISTRATION NO. (if appropriate)   38,663

TELEPHONE   303-379-1136   Docket Number: 20008.111P1US

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Certificate of Mailing under 37 CFR 1.10	Application Number	Applied For
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1.	Provisional Application For Patent Cover Sheet Form PTO/SB/16 (2 for a total of 2 pages)
2.	Abstract (1 page)
3.	Specification (53 pages)
4.	Claims (11 pages – 52 claims)
5.	Formal Drawings (21 sheets – 21 figures)
6.	Return Receipt Postcard

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20008.111P1US

IMPROVED ALD APPARATUS AND METHOD

References Cited:

5

U.S. PATENT DOCUMENTS

1. 4,058,430	11, 1977	Suntola et al.
2. 4,389,973	1, 1983	Suntola et al.
3. 4,413,022	11, 1983	Suntola et al.
4. 4,993,357	2, 1991	Scholz
5. 5,114,683	5, 1992	Hirase
6. 5,225,366	7, 1993	Yoder
7. 5,281,274	1, 1994	Yoder
8. 5,483,919	1, 1996	Yokoyama et al.
9. 5,711,811	1, 1988	Suntola et al.
10. 5,758,680	6, 1998	Kaveh et al.
11. 5,855,680	1, 1999	Soininen et al.
12. 5,928,426	7, 1999	Aitchison
13. 6,015,590	1, 2000	Suntola et al.
14. 6,174,377	1, 2001	Doering et al.
15. 6,305,314	10, 2001	Sneh et al.
16. 6,361,607	3, 2002	Dozoretz et al.
17. 6,447,607	9, 2002	Soininen et al.
18. 2002/0076508 A1	6, 2002	Chiang et al.
19. 10/347575	1, 2003	Sneh

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OTHER PUBLICATIONS

1. Ritala et al., in: H. S. Nalwa, (Ed), Handbook of Thin Film Materials, Academic Press, San Diego, 2001, Vol. 1, Chapter 2, p 103.
2. Sneh et al., *Thin Film Atomic Layer Deposition Equipment for Semiconductor Processing*, Thin Solid Films, 402/1-2 (2002) 248.

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ABSTRACT

35 Improved apparatus and method for SMFD ALD include a method designed to enhance chemical utilization as well as an apparatus that implements lower conductance out of SMFD-ALD process chamber while maintaining full compatibility with standard wafer transport. Improved SMFD source design from volatile and non-volatile liquid and solid precursors are disclosed.

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BACKGROUND OF THE INVENTION

1. Field of the invention

This invention relates to the field of atomic layer deposition ("ALD"), and

5   more particularly to apparatus and methods for performing ALD with high throughput and low cost.

2. Description of Prior Art.

Thin film deposition is commonly practiced in the fabrication of semiconductor devices and many other useful devices. An emerging deposition

10   technique, atomic layer deposition (ALD), offers superior thickness control and conformality for advanced thin film deposition. ALD is practiced by dividing conventional thin-film deposition processes into single atomic-layer deposition steps that are self-terminating and deposit precisely one atomic layer when conducted up to or beyond self-termination exposure times. An atomic layer

15   typically equals about 0.1 molecular monolayer to 0.5 molecular monolayer. The deposition of atomic layer is the outcome of a chemical reaction between a reactive molecular precursor and the substrate. In each separate ALD reaction-deposition step, the net reaction deposits the desired atomic layer and eliminates the "extra" atoms originally included in the molecular precursor.

20   In ALD applications, typically two molecular precursors are introduced into the ALD reactor in separate stages. For example, a metal precursor molecule, ML_x, comprises a metal element, M (e.g., M = Al, W, Ta, Si, etc.), that bonded to atomic or molecular ligands, L. The metal precursor reacts with the substrate. This ALD reaction occurs only if the substrate surface is prepared to react directly

25   with the molecular precursor. For example, the substrate surface typically is prepared to include hydrogen-containing ligands, AH, that are reactive with the metal precursor. The gaseous precursor molecule effectively reacts with all the ligands on the substrate surface, resulting in deposition of an atomic layer of the metal: substrate -AH + ML_x → substrate -AML_{x-1} + HL, where HL is a reaction by-

30   product. During the reaction, the initial surface ligands, AH, are consumed, and the surface becomes covered with L ligands, which cannot further react with metal

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precursor ML_x. Therefore, the reaction self-terminates when all of the initial AH ligands on the surface are replaced with AML_{x-1} species.

The reaction stage is typically followed by an inert-gas purge stage that eliminates the metal precursor from the chamber prior to the separate introduction 5 of the other precursor.

A second molecular precursor then is used to restore the surface reactivity of the substrate towards the metal precursor. This is done, for example, by removing the L ligands and redepositing AH ligands. In this case, the second precursor typically comprises the desired (usually nonmetallic) element A (i.e., O, 10 N, S), and hydrogen (i.e., H_2O, NH_3, H_2S). The reaction, substrate-ML + AH_y → substrate-M-AH + HL, (here, for the sake of simplicity, the chemical reactions are not balanced) converts the surface back to being AH-covered. The desired additional element, A, is incorporated into the film and the undesired ligands, L, are eliminated as volatile by-product. Once again, the reaction consumes the reactive 15 sites (this time, the L-terminated sites) and self-terminates when the reactive sites on the substrate are entirely depleted. The second molecular precursor then is removed from the deposition chamber by flowing inert purge-gas in a second purge stage.

This sequence of surface reactions and precursor-removal that restores the 20 substrate surface to its initial reactive state is a typical ALD deposition cycle. Restoration of the substrate to its initial condition is a key aspect of ALD. It implies that films can be layered down in equal metered sequences that are all identical in chemical kinetics, deposition per cycle, composition, and thickness. Self-saturating surface reactions make ALD insensitive to transport nonuniformity. This 25 transport nonuniformity may pertain either to the engineering and the limitations of the flow system or could be related to surface topography (i.e., deposition into three-dimensional, high-aspect ratio structures). Nonuniform flux of chemicals can only result in different completion times at different areas. However, if each of the reactions is allowed to complete on the entire substrate surface, the different 30 completion kinetics bear no penalty. This is because the areas that are first to complete the reaction self-terminate the reaction, while the rest of the area on the

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surface is able to complete the reaction and self-terminate and essentially catch up.

Efficient practice of ALD requires an apparatus capable of changing the flux of chemicals from ML_x into AH_y abruptly and fast. Furthermore, the apparatus

5   must be able to carry this sequencing efficiently and reliably for many cycles to facilitate cost-effective coating of many substrates. Typically, an ALD process deposits about 0.1 nm of a film per ALD cycle. A useful and economically feasible cycle time must accommodate a thickness in a range of about from 3 nm to 30 nm for most semiconductor applications, and even thicker films for other applications.

10   Industry throughput standards dictate that substrates be processed in 2 minutes to 3 minutes, which means that ALD cycle times must be in a range of about from 0.6 seconds to 6 seconds. Multiple technical challenges have so far prevented cost-effective implementation of ALD systems and methods for manufacturing of semiconductor devices and other devices.

15   Generally, an ALD process requires alternating in sequence the flux of chemicals to the substrate. A representative ALD process, as discussed above, requires four different operational stages:

1. ML_x reaction;

2. ML_x purge;

20   3. AH_y reaction; and

4. AH_y purge.

Given the need for short cycle times, chemical delivery systems suitable for use in ALD must be able to alternate incoming molecular precursor flows and purges with sub-second response times. Also, if significant flow nonuniformities exist, these can be overcome through the self-terminating nature of the chemical

25   reactions by increasing the reaction-stage time to the time dictated by areas that are exposed to the smallest flux. Nevertheless, this necessarily degrades throughput since cycle times increase correspondingly.

In order to minimize the time that an ALD reaction needs to reach self-

30   termination, at any given reaction temperature, the flux of chemicals into the ALD reactor must be maximized. In order to maximize the flux of chemicals into the

ALD reactor, it is advantageous to introduce the molecular precursors into the ALD reactor with minimum dilution of inert gas and at high pressures. On the other hand, the need to achieve short cycle times requires the rapid removal of these molecular precursors from the ALD reactor. Rapid removal in turn dictates that

5   gas residence time in the ALD reactor be minimized. Gas residence times, τ, are proportional to the volume of the reactor, V, the pressure, P, in the ALD reactor, and the inverse of the flow, Q, $\tau = VP/Q$. Accordingly, lowering pressure (P) in the ALD reactor facilitates low gas residence times and increases the speed of removal (purge) of chemical precursor from the ALD reactor. In contrast,

10 minimizing the ALD reaction time requires maximizing the flux of chemical precursors into the ALD reactor through the use of a high pressure within the ALD reactor. In addition, both gas residence time and chemical usage efficiency are inversely proportional to the flow. Thus, while lowering flow will increase efficiency, it will also increase gas residence time.

15   Existing ALD apparatuses have struggled with the trade-off between the need to shorten reaction times and improve chemical utilization efficiency, and on the other hand, the need to minimize purge-gas residence and chemical removal times. Certain ALD systems of the prior art contain chemical delivery manifolds using synchronized actuation of multiple valves. In such systems, satisfactory

20 elimination of flow excursions is impossible because valve actuation with perfect synchronization is itself practically impossible. As a result, the inevitable flow excursions are notorious for generating backflow of gas that leads to adverse chemical mixing.

        Thus, a need exists for an ALD apparatus that can achieve short reaction

25 times and good chemical utilization efficiency, and that can minimize purge-gas residence and chemical removal times, while preventing backflow.

        As a conventional ALD apparatus is utilized, "memory" effects tend to reduce the efficiency of the ALD reactor. Such memory effects are caused by the tendency of chemicals to adsorb on the walls of the ALD reactor and

30 consequentially release from the walls of the ALD reactor on a time scale that is dictated by the adsorption energy and the temperature of the walls. This

phenomenon tends to increase the residence time of trace amounts of chemicals in the ALD reactor. As a result, memory effects tend to increase the purge-time required for removal of chemicals. Thus, a need exists for an ALD apparatus that minimizes memory effects.

5　　　　　Films grow on all areas of conventional ALD apparatuses that are exposed to the chemicals. In particular, film growth occurs on exposed chamber walls, as well as on the substrate. Film growth on chamber walls deteriorates performance of the ALD apparatus to the extent that the growth of film produces an increased surface area on the walls of the ALD chamber. The propensity of films to grow on

10　the chamber walls scales with the surface area of the chamber walls. Likewise, increased surface area further extends chamber memory effects. An increase in surface area may result from the growth of inferior porous film deposits. Film growth that results in porous deposits can extend chamber memory by entrapments of chemical molecules inside the pores. Thus, it is essential to the

15　functioning of an ALD apparatus that growth of films and deposits is kept to a minimum, and that any film growth that does occur is controlled to deposit high quality films that effectively cover the walls without an increase of surface area or the growth of porosity. Thus, a further need exists for an ALD apparatus that minimizes film growth and provides for the control of any film growth that is allowed

20　to occur.

　　　　　A well optimized ALD apparatus and method is designed to maintain adequate chemical separation in the reaction space that directly impacts the flux of chemicals on the substrate, named the ALD space. Accordingly, adverse coexistence of ALD precursor is characteristic for the system space downstream

25　from the ALD space. To avoid this coexistence, one must significantly sacrifice the throughput of the ALD system (in order to adequately purge substantially larger volume). Typically, ALD precursors coexisting in a chamber space tend to produce inferior films. Accordingly, throughput optimized ALD systems suffer from the tendency to grow inferior solid deposits in the space just downstream to the

30　ALD space. Inferior film growth tends to go out of control since increased surface area enhances precursor coexistence that quickly aggravates the problem by a

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positive feedback mechanism. Since some of the chemicals at the downstream vicinity to the ALD space is destined to transport back into the ALD space (e.g., by diffusion), ALD peak performance will deteriorate. In addition, inferior deposition of particles on the substrate will be promoted. Accordingly, conventional ALD
5   systems operated at peak throughput are doomed for fast degradation of ALD and contamination performance.

Since, as explained above, throughput optimized ALD systems are defined by an inevitable precursor coexistence right downstream to the ALD space, maintaining these systems at peak performance over long and cost effective
10   maintenance cycles dictates that the unavoidable downstream deposition of films will be actively controlled for adequate quality and preferred location. An additional benefit of localized precursor abatement downstream from the ALD space is obtained by substantially reducing wear of downstream components such as pumps, valves, and gauges.
15   Cold and hot traps were extensively used to remove undesired constituents from downstream effluents, in the sub-atmospheric pressure range, and are well known to those who are skilled in the art. Other techniques were also proven to be effective for this purpose such as plasma abatement apparatuses and residence time extending traps. Many of these abatement solutions are available in the
20   commercial market as "turn-key" equipment that can be adapted for effective use on a variety of different systems. Typically, these abatement apparatuses implement sacrificial abatement surfaces for effectively trapping reactive constituents either permanently (e.g., by chemical reaction to deposit solid films) or temporarily. A majority of these traps can be adapted, in principle, into the
25   downstream of ALD systems. However, considerations of safety and the need to seamlessly integrate abatement into an optimized ALD system considerably restrict the effectiveness and cost effectiveness of most abatement techniques.

ALD generally is advantageous over other deposition techniques in that gas-flow and gas-pressure nonuniformities during chemical dosages do not
30   necessarily cause film nonuniformities, provided that appropriately long dose times are implemented. However, gas entrapment and gas-flow disturbances could

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severely and adversely impact the effectiveness of purge steps. For example, the "dead-leg" space associated with the wafer transport channel in the wall of a single wafer processing chamber is a known problem in the art of wafer processing such as chemical vapor deposition (CVD), etch, ALD, and PVD. In particular, effective

5   ALD purge of this space is typically impossible. The art of single wafer deposition presents a variety of effective remedies for this problem. For example, U.S. Patent No. 5,558,717 teaches the advantageous implementation of an annular flow orifice and an annular pumping channel. This annular design requires a relatively wide process-chamber design.   In another example, U.S. Patent No. 6,174,377

10   describes an ALD chamber designed for wafer loading at a low chuck position, while wafer processing is carried out at a high chuck position, leaving the wafer transport channel, and the flow disturbances associated with it, substantially below the wafer level. Both of these prior art solutions and other prior art solutions are not ideally suited to resolve the slot valve cavity problem in ALD systems.

15   Thus, a need exists in chemical deposition processes, particularly in ALD technology, for an apparatus that provides uniform and symmetrical flux of chemicals to substrate surfaces, and provides smooth flow-path structures without dead-leg wafer loading cavities.

      In previous patent applications by the inventor of this invention, US Patent

20   Application No. 10/347575 and PCT Application No. US03/01548, embodiments that helped solve some of the problems described above were disclosed. Systems, apparatuses, and methods in accordance with that invention provide Synchronous Modulation of Flow and Draw ("SMFD") in chemical processes, and in particular, in atomic layer deposition processes and systems. These patent

25   applications are included here as references.

      Atomic layer deposition ("ALD") is preferably practiced with the highest possible flow rate through the deposition chamber during purge, and with the lowest possible flow rate during dosage of chemicals. Accordingly, an efficient ALD system in accordance with US Patent Application No. 10/347575 and PCT

30   Application No. US03/01548 is able to generate and accommodate significant modulation of flow rates. Under steady-state conditions, the flow of process gas

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(either inert purge gas or chemical reactant gas) into a chamber, referred to herein as "flow", matches the flow of gas out of a chamber, referred to herein as "draw".

An important aspect of an embodiment in accordance with the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548 is that it resolves the trade-off in conventional ALD systems between the contradictory requirements of a high flow rate during a purge of the deposition chamber and of a low flow rate during chemical dosage. SMFD in accordance with that invention provides the ability to purge a process chamber at a low-pressure and a high purge-gas flow rate, and sequentially to conduct chemical dosage in the process chamber at a high-pressure and a low flow rate of chemical reactant gas, and to modulate pressures and gas flow rates with fast response times.

In one aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a method of conducting atomic layer deposition includes conducting a first chemical dosage stage, the first chemical dosage stage comprising flowing a first chemical reactant gas through a deposition chamber at a selected first-dosage flow rate and at an independently selected first-dosage pressure, then conducting a purge stage by flowing purge gas through the deposition chamber at a selected purge flow rate and at an independently selected purge pressure, then conducting a second chemical dosage stage, the second chemical dosage stage comprising flowing a second chemical reactant gas through the deposition chamber at a selected second-dosage flow rate and at an independently selected second-dosage pressure, and then conducting a purge stage by flowing purge gas through the deposition chamber at a selected purge flow rate and at an independently selected purge pressure. Generally, the purge flow rate is greater than the first-dosage and second-dosage flow rates, the ratio of the purge flow rate to the dosage flow rate typically exceeding 1.5, usually exceeding 20, and preferably exceeding 100.

In another aspect of the invention of US Patent Application No. 10/347575 and PCT Application No. US03/01548, initiating the first chemical dosage stage includes initially flowing the first chemical reactant gas at a first transient flow rate, the first transient flow rate being initially substantially greater than the first-dosage

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flow rate, and initiating the second chemical dosage stage includes initially flowing the second chemical reactant gas at a second transient flow rate, the second transient flow rate being initially substantially greater than the second-dosage flow rate.

5   In another aspect of US Patent Application No. 10/347575 and PCT Application No. US03/01548, flowing a first chemical reactant gas at a selected first-dosage flow rate and at an independently selected first-dosage pressure includes controlling the first-dosage flow rate of the first chemical reactant gas into the deposition chamber and independently substantially matching a first-chemical

10   draw of the first chemical reactant gas out of the deposition chamber to the first-dosage flow rate. In still another aspect of that invention, flowing a second chemical reactant gas at a selected second-dosage flow rate and at an independently selected second-dosage pressure includes controlling the second-dosage flow rate of the second chemical reactant gas into the deposition chamber

15   and independently substantially matching a second-chemical draw of the second chemical reactant gas out of the deposition chamber to the second-dosage flow rate. In still another aspect of that invention, flowing purge gas through the deposition chamber at a selected purge flow rate and at an independently selected pressure includes controlling the purge flow rate of the purge gas into the

20   deposition chamber and independently substantially matching a purge-draw of the purge gas out of the deposition chamber to the purge flow rate.

In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, matching the first-chemical draw of the first chemical reactant gas out of the deposition chamber includes controlling

25   a first-dosage draw pressure downstream from the deposition chamber, and matching the second-chemical draw of the second chemical reactant gas out of the deposition chamber includes controlling a second-dosage draw pressure downstream from the deposition chamber. In another aspect of that invention, matching the purge-draw of the purge gas out of the deposition chamber includes

30   controlling a purge-draw pressure downstream from the deposition chamber.

In yet another modification of the invention described in US Patent

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Application No. 10/347575 and PCT Application No. US03/01548, flowing a chemical reactant gas or a purge gas at a selected flow rate and at an independently selected pressure includes controlling the flow rate into the deposition chamber and intentionally controlling the draw out of the deposition

5   chamber to mismatch the flow rate going into the deposition chamber by controlling a draw pressure downstream from the deposition chamber. As a result, the pressure in the deposition chamber substantially changes to substantially correct the mismatch between flow and draw and to substantially match the draw to the flow following a transient period. Accordingly, dose and purge steps can be

10   carried at substantially different pressures. .

In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, controlling the first-dosage draw pressure, the second-dosage draw pressure, and the purge-draw pressure includes flowing draw gas at a draw-gas flow rate through a draw control chamber

15   and controlling the draw-gas flow rate to achieve a desired draw pressure, the draw control chamber being located downstream from the deposition chamber.

In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, controlling the first-dosage flow rate into the deposition chamber includes providing a first reactant-gas source

20   having a known first-source pressure, and flowing first chemical reactant gas from the first reactant-gas source through a first-source Flow Restricting Element ("FRE") into the deposition chamber, and controlling the second-dosage flow rate into the deposition chamber includes providing a second reactant-gas source having a known second-source pressure and flowing second chemical reactant

25   gas from the second reactant-gas source through a second-source FRE into the deposition chamber, and controlling the purge flow rate into the deposition chamber includes providing a purge-gas source having a known purge-source pressure and flowing purge gas from the purge-gas source through a purge-source FRE into the deposition chamber.

30   In still another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a method in accordance

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with that invention also includes filling a first booster chamber with first chemical reactant gas at substantially the known first-source pressure during a time period not including the first chemical dosage stage, the first booster chamber being located downstream from the first-source FRE and upstream from the deposition

5 chamber, and initiating the first chemical dosage stage by opening a first chemical shut-off valve, the first chemical shut-off valve being in serial fluidic communication between the first booster chamber and the deposition chamber, thereby initially flowing the first chemical reactant gas at a first transient flow rate, the first transient flow rate being initially substantially greater than the first-dosage flow rate, and

10 filling a second booster chamber with second chemical reactant gas at substantially the known second-source pressure during a time period not including the second chemical dosage stage, the second booster chamber being located downstream from the second-source FRE and upstream from the deposition chamber, and initiating the second chemical dosage stage by opening a second

15 chemical shut-off valve, the second chemical shut-off valve being in serial fluidic communication between the second booster chamber and the deposition chamber, thereby initially flowing the second chemical reactant gas at a second transient flow rate, the second transient flow rate being initially substantially greater than the second-dosage flow rate.

20 In one aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a system in accordance with the invention is able to modulate synchronously the residence time and pressure of gas in a process chamber. The word "synchronously" in that invention means in rapid controlled succession, with fast response times and with minimal

25 uncontrolled excursions of pressure or gas flow rate. A system in accordance with that invention includes an apparatus capable of modulating a flow of gas into a process chamber ("PC"), and substantially concurrently and independently matching a draw of the gas out of the PC to the flow to sustain a substantially steady pressure throughout the deposition while substantially modulating the flow

30 and residence time of gas in the PC. Accommodating large flow modulations enables independent optimization of purge and dose and comprises the major

benefit of SMFD implementation. However, some limited intentional pressure modulation, in particular an advantageous pressure increase during chemical dose, can also be implemented, in addition to the flow modulation. Such pressure modulations are achieved if draw modulation synchronously with flow modulation

5 is provided with some predetermined mismatch. This mismatch, while in a well-designed SMFD apparatus and method does not induce backflow, causes the pressure in the PC to correctively transient to reach flow-draw match resultantly and effectively in synchronous designed pressure modulation. Thus, in another aspect of that invention, a system includes a process chamber, a process-gas

10 conduit connected to the process chamber for controlling a flow rate of gas into the PC, a draw control chamber ("DC") configured for a flow of draw gas, a process-chamber flow restriction element ("FRE") in serial fluidic communication between the PC and the DC, a draw exhaust line in fluidic communication with the DC and a draw FRE in serial fluidic communication with the draw exhaust line. Generally, an

15 FRE is designed to provide a certain conductance (or inversely, resistance) in a gas flow path. In another aspect of that invention, a system further includes a draw-gas shut-off valve to control a flow of draw-gas through the DC. In still another aspect of that particular invention, a system includes a draw-source-FRE in serial fluidic communication with the draw-gas shut-off valve and the DC. In

20 another aspect, a system further includes a plurality of process-gas shut-off valves in serial fluidic communication with the process-gas conduit, each shut-off valve being configured to control the inflow of a process gas into the process chamber. In another aspect, one of the process-gas shut-off valves comprises a purge-gas shut-off valve in fluidic communication with the PC for controlling the flow of a

25 purge gas to the PC. In another aspect, a system further includes a purge-source FRE in serial fluidic communication with the purge-gas shut-off valve. In another aspect, a system further includes a plurality of process-gas FREs, each process-gas FRE being in serial fluidic communication with one of the process-gas shut-off valves. In another aspect, a system further includes a plurality of booster

30 chambers, each booster chamber being in serial fluidic communication with the process-gas conduit, each booster chamber being located upstream from one of

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the process-gas shut-off valves and downstream from one of the process-gas FREs. In another aspect, a system further includes a plurality of booster FREs, each booster FRE being downstream from one of the booster chambers. In another aspect, a system further includes a gas distribution chamber in serial

5   fluidic communication between the process-gas shut-off valves and the PC and in serial fluidic communication between the purge gas shut-off valve and the PC, and a gas-distribution FRE in serial fluidic communication between the gas distribution chamber and the PC. In another aspect, a system further includes a purge-exhaust line in fluidic communication with the gas distribution chamber, and a

10   purge exhaust shut-off valve, the purge exhaust shut-off valve being in serial fluidic communication between the gas distribution chamber and the purge-exhaust line. In another aspect, a system further includes a purge-exhaust FRE in serial fluidic communication with the purge exhaust shut-off valve. In another aspect, some of the process-gas shut-off valves comprise a multi-way valve having a plurality of

15   non-common ports and a plurality of common ports, each of the non-common ports being in serial fluidic communication with a process-gas source, a plurality of common ports being in serial fluidic communication with the PC, and at least one common port being in serial fluidic communication with the purge gas shut-off valve.

20   In some preferred embodiments of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, an apparatus further includes a draw-gas introduction chamber ("DGIC"), the DGIC being in serial fluidic communication between the PC and the DC, a draw-gas shut-off valve to control a flow of draw-gas into the DGIC, a process-chamber FRE located

25   between the PC and the DGIC, and a DGIC-FRE located between the DGIC and the DC. In another aspect, a system further includes a draw-source-FRE located in serial fluidic communication with the draw-gas shut-off valve and the DGIC.

In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a system further includes an

30   abatement surface located in the DC. In still another aspect, a system further includes a reactive gas inlet for introducing reactive gas into the DC to enhance

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chemical abatement. In another aspect, the reactive gas inlet comprises a reactive gas plenum proximate to the DC. In another aspect, a system further includes an abatement chamber, the abatement chamber located downstream from the DC.

5   In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a system further includes a pressure control chamber located downstream from the DC and in serial fluidic communication with the DC and the draw exhaust line. In another aspect, the PC is an atomic layer deposition chamber ("ALDC").

10   In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a system in accordance with the invention includes a reactor vessel having a reactor-vessel wall and a vessel interior, wherein the deposition chamber, the DGIC, and the DC are enclosed in the vessel interior.

15   In another aspect of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, a system in accordance with the invention includes a reactor vessel containing a perimeter slot valve ("PSV"), whereby the PSV includes a substrate-transport slot through the reactor-vessel wall, a continuous perimeter cavity within the reactor-vessel wall, a continuous sealing poppet, and an actuator for moving the sealing poppet between an open

20   position and a closed position, wherein the sealing poppet is moved into the perimeter cavity in the closed position, the sealing poppet is moved out of the perimeter cavity in the open position, the substrate-transport slot is substantially coplanar with a substrate-supporting surface of a substrate holder, the perimeter cavity is substantially coplanar with the substrate-transport slot, the substrate-

25   transport slot defines a substrate-transport channel through the reactor-vessel wall to the substrate holder when the sealing poppet is in the open position, and the sealing poppet separates the substrate-transport slot from the vessel interior when the sealing poppet is in the closed position.

      In some embodiments of the invention described in US Patent Application

30   No. 10/347575 and PCT Application No. US03/01548, pressure in the PC (or ALD chamber) is maintained substantially constant during synchronous flow-draw

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modulation. In other embodiments in accordance with that invention, throughput and material utilization are further improved by conducting one or more chemical-dosage stages at higher pressures. For example, in some embodiments, the pressure during purge is maintained in a range of about from 30 mTorr to 100

5   mTorr, while ALD-pressure during chemical dosage is maintained in a range from 200 mTorr to 1000 mTorr.

Atomic layer deposition ("ALD") is preferably practiced with the highest possible flow rate through the deposition chamber during purge, and with the lowest possible flow rate during dosage of chemicals. Accordingly, an efficient

10   ALD system is able to generate and accommodate significant modulation of flow rates. Under steady-state conditions, the flow of process gas (either inert purge gas or chemical reactant gas) into a chamber, referred to herein as "flow", matches the flow of gas out of a chamber, referred to herein as "draw".

To accommodate significant flow modulations, a system in accordance with

15   the invention of US Patent Application No. 10/347575 and PCT Application No. US03/01548 is capable of substantially matching the flow and the draw. For example, a representative ALD cycle includes a sequence of chemical A dosage, A purge, chemical B dosage, and B purge at gas flow rates of 10 sccm, 1000 sccm, 5 sccm, and 1000 sccm, respectively. Process pressure is maintained

20   substantially steady if the draw is controlled to modulate synchronously at substantially the same flow rate.

If modulations of the draw did not substantially match flow modulations, the process system would not be able to maintain process pressure. As a result, the system would inevitably transient into higher pressure during a purge stage, and

25   then into a lower pressure during a chemical dosage stage.

Flow into a deposition or other type of PC is generally controlled using an upstream manifold, substantially independent of process pressure. Draw is determined by the conductance of the PC outlet, C_{PC}, and by the pressure differential across that outlet, $\Delta P = P_{PC} - P_{Draw}$. Accordingly, draw $= C_{PC}\Delta P$. Draw

30   modulations can be achieved by modulating the conductance, C_{PC}, or the pressure differential, ΔP, or both. Modulating conductance out of PCs is commonly used in

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the art of process flow systems, such as CVD, PVD, and etch systems, using mechanical devices named throttle valves. While throttle valves have been adequately used to control steady-state pressure in those systems, they are currently too slow to accommodate the fast response times required in SMFD

5   systems. In addition, throttle valves cause undesirable flow disturbance and generate particles. To circumvent flow distortion and particle generation problems, throttle valves are typically conventionally utilized at a downstream location that is significantly remote from the process zone. However, efficient ALD system design requires minimized ALD chamber volume forcing the location of draw control to the

10   vicinity of the substrate. Other means to modulate conductance, such as changing the temperature of the process outlet, are rather limited in range and very slow. Finally, draw modulation may be achieved by modulating the pumping speed of a vacuum pump. Significant pumping speed modulation, however, responds slowly and also significantly wears out the pump if attempted at desired ALD switching

15   rates.

Best suited for modulation of drawing in accordance with the invention of US Patent Application No. 10/347575 and PCT Application No. US03/01548, therefore, is ΔP modulation. Modulation of ΔP while maintaining PC pressure, P_{PC}, substantially constant is practiced in accordance with the invention by modulating

20   P_{Draw}. For example, a DC is located downstream from the PC, and said DC has an outlet with conductance C_{Draw}. By flowing control gas into and through the DC, P_{Draw} can be controlled independently of the pressure, P_{PC}, in the PC or deposition chamber upstream. The flow of gas into the DC is the total of the draw from the PC and the directly inserted draw gas flow. Since the draw is a function of ΔP,

25   independent control of ΔP provides substantial matching of draw to flow independent of the flow. Since, in principle, draw chambers can be made very small, modulation of ΔP can be practiced with sub-millisecond speed. While certain embodiments of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548 might be advantageously

30   implemented with small volume DCs to facilitate process conditions with short and rather negligible transient times, it is also possible to advantageously sacrifice

draw control speed to provide substantially larger DCs. Accordingly, DCs with several liters of volume are the ideal space for controlling chemical trapping or abatement process. For example, DC response in the range of from 10 msec to 20 msec is compromised in a typical 200 mm wafer deposition system for the

5 benefit of about 3 liter of usable DC space. While, as explained below, this "slower" draw response is destined to create some unavoidable 5% − 15% of typical PC pressure modulations at the end of a chemical dose stage, it is tested both practically and theoretically to have negligible impact on ALD performance. Unavoidable process pressure modulations are related to the difference between

10 typically 2 msec to 4 msec time response of the ALD chambers to the onset of high purge flow and the longer chosen response of the DC. In certain embodiments, if both a fast responding DC and a large volume abatement chamber are necessary, abatement is directed, as explained in US Patent Application No. 10/347575 and PCT Application No. US03/01548, to an additional chamber located downstream to

15 the DC. In this case, since the pressure drop on the draw chamber FRE is preferably large, residence times in the additional abatement chamber are kept adequately long using large volume abatement chamber. For example, if the pressure drops by a factor of 10 over the draw chamber FRE, the abatement chamber must be 10 times larger to provide similar effective abatement, typically

20 10 liters to 50 liters instead of 1 liter to 5 liters. This size comparison explains the benefit of compromising ideal SMFD performance, which is believed to be adequate in most cases, for the prospects of trapping or abating chemicals in the DC. Additionally, if draw chambers are being used for the sole purpose of draw control (meaning they are very small), care should be taken to extend ALD

25 standard purge to include the DC to ensure that inferior film growth cannot take place in the DC. This necessity has negligible throughput penalty (provided that the draw chamber flow path is well designed and the draw chamber walls are controlled to an appropriate temperature) since these chambers can be made, for the typical 200 mm wafer system, with a volume of 30 cc to 70 cc and are also

30 subjected during chemical dose to a very small partial pressure of chemicals, since the high draw flow essentially acts to dilute the chemicals during chemical dose.

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Response time of ΔP-modulation is directly related to response time of P_{DC} modulation, and depends on the draw control volume, the conductance of the draw control outlet, and the flow.

5   Consistent delivery of ALD precursors has been key for successful optimized ALD. As one of its greatest advantages, ALD does not mandate stringent chemical delivery consistency. However, the impact of inconsistent precursor delivery must be circumvented with excessive dosage to ensure saturation at the lowest point of a fluctuating chemical delivery. As a result, material utilization and subsequently maintainability are adversely impacted by the

10   need to effectively dose more precursors. Accordingly, it is beneficial for optimized ALD to rely on consistent delivery of chemicals. As sensitivity to chemical delivery consistency is greatly reduced, compared to CVD, typically better than $\pm 5\%$ consistency is proven to be sufficient.

Consistent delivery of gas chemicals has been practiced in the art with great

15   success. The delivery of precursors from liquid and solid sources was practiced by seeding the vapor of chemicals into the flow of a typically inert carrier gas. This method has been only marginally successful due to the interdependence of seed concentration and flow. In particular, seeded gas chemical delivery systems suffer from slow and inconsistent start and stop transients. In several cases, this makes

20   them perform most poorly in ALD applications. The introduction of liquid precursors into a CVD reactor was practiced by direct liquid delivery and vaporization. However, this technique is not suitable for ALD, since neither liquid delivery nor vaporization can be alternated fast enough and cannot be controlled to deliver abruptly and intermittently such small quantities that are useful for cost-

25   effective ALD.

Consistent delivery of precursors from solid materials has been unreliable due to the difficulty to maintain a stable vapor pressure, especially under conditions of changing flow (associated, for example, with the start and stop of the process in the case of CVD and with the chemical pulsation required for ALD).

30   Sublimation sources were employed to evaporate the solid by controlling the temperature. The main difficulties were maintaining efficient vaporization under

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transients, supplying chemicals to the source, maintenance, and end-point detection.

There is a need to improve SMFD-ALD apparatus and method by providing improved definition of process chamber and further implementing methods that

5 enhance chemical utilization efficiencies. There is also a need to provide SMFD-ALD optimized chemical source designs especially for the efficient and consistent delivery of vapor from low-volatility liquid and solid chemicals.

SUMMARY OF THE INVENTION

Embodiments in accordance with the invention provide improved apparatus

10 and method to further enhance the advantages of SMFD-ALD apparatus and method. In one embodiment, the invention provides a method of conducting atomic layer deposition with enhanced material utilization efficiency. In that method, chemical dosage is conducted in a dose and hold mode. During the hold mode, the flow of chemical into the process chamber is terminated while the flux is

15 effectively maintained. This mode is beneficial for the final stages of chemical dose where chemical depletion is minimal, while maintaining chemical flux can further promote the reaction far into saturation to much improve film quality.

In some embodiments of the invention, a chemical dose stage includes flowing a chemical reactant gas to substantially and rapidly fill up the deposition

20 chamber. The rapid introduction of chemical is followed by substantially reducing the flow of the chemical reactant gas while concurrently reducing the flow out of the deposition chamber by increasing the pressure downstream to the deposition chamber to substantially match the flow out of the deposition chamber to the chemical reactant gas flow into the deposition chamber. At a certain specified time

25 after the start of the chemical dose step, the flow of the chemical into the deposition chamber is terminated while the pressure downstream from the deposition chamber is substantially matched to the pressure in the deposition chamber to substantially suppress and to virtually eliminate the flow out of the deposition chamber. The dose is extended from that point for a specified time

30 without further introduction of chemical flow.

The invention teaches a method for controlling the pressure downstream to

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the deposition chamber by flowing gas into a draw gas introduction chamber (DGIC) located in serial fluidic communication downstream from the deposition chamber in relation to embodiments for the dose and hold method that is presented as an improvement and enhancement in context to the apparatus and

5   method for SMFD-ALD.

Improved ALD performance is also described in terms of apparatus and method to utilize a perimeter slot valve as a means to control and reduce the conductance out of the ALD process chamber for the purpose of increasing the pressure gradient over the flow restriction element located between the process

10   chamber and a subsequent draw chamber or DGIC which is proven to be advantageous for SMFD-ALD performance. This gap-controlling perimeter slot valve (PSV) is exemplified and illustrated in details within several preferred embodiments and associated drawings. An SMFD-ALD system including a PSV has a substrate holder made larger than the substrate. The perimeter area of the

15   substrate holder is not covered by the substrate. The sealing poppet of the PSV creates a substantially radial narrow gap between the uncovered perimeter area of the substrate holder and the bottom surface of the poppet when the PSV is in closed position. That radial narrow gap is narrower than the substrate transport slot when the PSV is in closed position and is equal to or wider than the substrate

20   transport slot when the PSV is in the open position.

The invention further teaches and clearly illustrates in the preferred embodiment description and drawings that the bottom surface of the poppet is advantageously designed with a substantially down-looking convex shape to minimize flow disturbances.

25   Enhanced maintainability of gap-controlling PSV according to another embodiment presented in this invention introduces a purge gas at substantially low flow between the fixed upper sealing surface and the upper poppet sealing surface of the PSV. This purge gas is supplied during processing and protects the inevitable crevice between the poppet and the associated sealing surface from

30   chemical entrapment and the growth of inferior film.

Enhanced maintainability of gap-controlling PSV according to yet another

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embodiment presented in this invention utilizes a radial inflatable seal formed between the fixed upper sealing surface and the upper poppet sealing surface of the gap-controlling PSV. According to this embodiment, the inflatable seal is placed in the gap between the poppet and the corresponding sealing surface,

5 downstream from the upper peripheral radial seal. The seal is inflated when the PSV is closed to substantially close and eliminate the gap downstream from the upper peripheral seal between the fixed upper sealing surface and the upper poppet sealing surface. In a further enhancement, the inflatable seal is made from a slightly permeable polymer, and the inflatable seal is inflated with high purity inert

10 gas. The minimal area of the inflated seal that is located between the fixed upper sealing surface and the upper poppet sealing surface and is exposed to the process is therefore substantially purged by the flow of the high purity inert gas out of the inflated seal. That flow can be maintained very low to effectively have no distinguishable impact on SMFD-ALD performance. In another variation in

15 accordance with the teaching of this invention, the inflatable seal is made from a perforated polymer and the inflatable seal is inflated with high purity inert gas. The minimal area of the inflated seal that is located between the fixed upper sealing surface and the upper poppet sealing surface and is exposed to the process is substantially purged by the flow of said inert gas out of the inflated seal.

20 The invention also discloses a semi-PSV (SPSV) apparatus for enhancing SMFD-ALD performance. Accordingly, the SPSV includes a substrate-transport slot through the reactor-vessel wall, a continuous perimeter cavity within the reactor-vessel wall, a continuous sealing poppet, and an actuator for moving the sealing poppet between an open position and a closed position. The sealing

25 poppet is moved into the perimeter cavity in the closed position and out of the perimeter cavity in the open position. The substrate-transport slot is substantially coplanar with a substrate-supporting surface of the substrate holder, and the perimeter cavity is substantially coplanar with the substrate-transport slot. The substrate-transport slot defines a substrate-transport channel through the reactor-

30 vessel wall to the substrate holder when the sealing poppet is in the open position. The sealing poppet separates the substrate-transport slot from the vessel interior

when the sealing poppet is in the closed position.

Specifically, the SPSV further includes a chamber top, a flexible metal bellow seal allowing the chamber top to move up and down while maintaining vacuum seal, a fixed lower sealing surface, a lower poppet sealing surface

5   corresponding to the fixed lower sealing surface, and a lower peripheral seal. The lower sealing surface and the peripheral seal are configured to seal the vessel interior when the sealing poppet is in the closed position. At that position, the poppet essentially defines the top portion of the vessel. The substrate holder is larger than the substrate, and the perimeter area of the substrate holder is not

10   covered by the substrate. The sealing poppet creates a substantially radial narrow gap between the uncovered perimeter area of the substrate holder and the bottom surface of the poppet. This radial narrow gap is narrower than the substrate transport slot when the SPSV is in the closed position and is equal or wider than the substrate transport slot when the SPSV is in the open position. The chamber

15   top can include a gas distribution showerhead. The design advantageously enhances SMFD-ALD by providing reduced conductance from the process chamber into the draw chamber or the DGIC. In one advantageous embodiment, the entire ALD manifold is mounted on the moving top of the SPSV and connected to the process gas and chemical sources with flexible means.

20   Further improvements in accordance with the present invention achieve lower conductance from the process chamber to a draw chamber or a DGIC by implementing a gap-controlling flexible diaphragm located behind a small inflation chamber. A ring-shaped and substantially radially-shaped diaphragm is positioned above the perimeter area of the substrate holder that is not covered with the

25   substrate. The inflated diaphragm moves towards the perimeter area of the substrate holder to reduce the gap between the diaphragm and the substrate holder and therefore reduce the conductance out of the process chamber. When the diaphragm is deflated for the purpose of wafer transport, the gap between the diaphragm and the substrate increases to accommodate the transport of the

30   substrate.

The diaphragm is made from an elastomer material. In another

embodiment, the elastomer material is perforated or slightly permeable and the diaphragm is inflated with pure inert gas. When the diaphragm is inflated, a slow flow of the inert gas emerges from the diaphragm surface into the process chamber to effectively purge the area of the diaphragm and protect the diaphragm

5   from the process.

In another design, the diaphragm is made from a metallic alloy and the diaphragm is pulled into the inflation chamber with a tension spring as described and illustrated. The metallic diaphragm is maintained in a down-looking concave-shaped position by the tension of that spring when the diaphragm is not inflated.

10   The diaphragm is inverted from a down-looking concave surface into a down-looking convex surface protruding into the vessel when the diaphragm is inflated. In the inflated state, the inflation pressure is able to overcome the tension of the spring (or multiple springs).

Improvements are also disclosed for SMFD optimized source design.

15   Principles for generic source design are implemented with commercially available pressure controller for volatile chemicals and with the aid of newly invented apparatuses for lower-volatility chemicals. A chemical vapor source for SMFD-ALD apparatus includes a chemical container, a pressure controller in serial fluidic communication downstream from the chemical container, and a source chamber in

20   serial fluidic communication downstream from the pressure controller. The pressure controller is located in serial fluidic communication upstream from the source chamber. The set pressure of the chemical vapor is maintained in the source chamber by the pressure controller. In one exemplary embodiment, the chemical source capacity exceeds the capacity loss per ALD cycle by a factor of

25   10. In another exemplary embodiment, the chemical source capacity exceeds the capacity loss per ALD cycle by a factor of 100.

Further, the invention discloses a chemical vapor source for an SMFD-ALD apparatus comprising a liquid delivery system, a vaporizer in serial fluidic communication downstream from that liquid delivery system, and a source

30   chamber in serial fluidic communication downstream from the vaporizer. A set chemical vapor pressure inside the source chamber is maintained by controlling

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the liquid delivery into the vaporizer. The chemical vapor pressure is measured in the source chamber, and the liquid delivery system is controlled to maintain that pressure at the set point. Therefore, the precision and response of the pressure control depends on the precision of the liquid delivery system and its ability to

5   respond quickly. In one exemplary embodiment, the chemical source capacity exceeds the capacity loss per ALD cycle by a factor of 10. In another exemplary embodiment, the chemical source capacity exceeds the capacity loss per ALD cycle by a factor of 100.

Further, an advantageous embodiment for a liquid delivery apparatus is

10   disclosed, exemplified, and illustrated for clarity. Accordingly, a controlled flow of liquid through a proportional valve is driven by an expandable pressure chamber. The expansion of that expandable pressure chamber protrudes into a liquid filled chamber. The pressure chamber is separated from the liquid filled chamber with an expandable flexible metallic bellow. When the pressure chamber is inflated, it

15   expands the bellow into the liquid-filled chamber to effectively pressurize the liquid and trigger the flow. The inflation or deflation operations are controlled with a fast solenoid-based valve and the introduction or disposition of air pressure, respectively. Accordingly, liquid flow can be triggered ON or OFF with unprecedented speed typically in the range of from 5 msec to 50 msec response

20   time.

In yet another embodiment, a pressure controlled chemical source utilizes a sublimation chamber that is connected in serial fluidic communication to a vaporizer, and the vaporizer is connected in serial fluidic communication with a source chamber, and the source chamber is connected in serial fluidic

25   communication to an SMFD-ALD manifold. The sublimation chamber is loaded with solid chemical and the chemical is subsequently sublimed from the sublimation chamber to condense on the wall area of the vaporizer. The desired vapor pressure of the solid chemical is maintained in the vaporizer and the source chamber corresponding to the vapor pressure of the solid chemical at the

30   temperature that is well maintained at the vaporizer. Most importantly, the wall area of the vaporizer is substantially high to substantially maintain the desired

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vapor pressure when the chemical is being utilized for SMFD-ALD process. The higher the area of the vaporizer, the better it can handle a draw out of chemical vapor, since the rate of vaporization scales with the area. However, the equilibrium between vapor and solid above the solid chemical condensed on the

5   vaporizer wall area ensures stabilized pressure independent of transient in the draw-out of vapor. This design is extremely stable, since it relies upon the temperature to set up the vapor pressure and maintains a constant temperature, while a conventional sublimation source must elevate the temperature to handle the draw of chemical vapor out of the source. Changing temperature as is carried

10   out in prior art is slow and difficult to control without overshooting.

The conductance through the vaporizer from the sublimation chamber into the source chamber and the temperature of the sublimation chamber during sublimation of that solid chemical out of the sublimation chamber to promote condensation onto the wall area of the vaporizer provides for effective

15   condensation of substantially all of the solid chemical over the vaporizer wall area as the vapors of sublimed chemical propagate through the vaporizer. Advantageously, condensation and buildup of the solid chemical over the wall area of the source chamber is substantially prevented, since the path through the vaporizer virtually condenses most of the chemical on the wall area of the

20   vaporizer. In one exemplary embodiment, the chemical source capacity exceeds the capacity loss per ALD cycle by a factor of 10. In another exemplary embodiment, the chemical source capacity exceeds the capacity loss per ALD cycle by a factor of 100.

Further improvement is achieved in accordance with the present invention

25   by loading the solid chemical into the sublimation chamber with a slurry of fine powder (the chemical) and inert liquid (inert removable additive). The liquid has a low boiling temperature so the solid chemical does not substantially dissolve in that liquid. Following, the inert liquid is vacuum-evaporated away from the chemical source to effectively leave a pure and dry solid chemical inside the sublimation

30   chamber. That consistent chemical source from a solid chemical is advantageous for general delivery of chemical from solid into a CVD process chamber.

A method is disclosed to enhance the safety of solid chemical delivery into and out of a chemical source by immersing the solid material in a non-solvating inert liquid with low boiling temperature to effectively protect the reactive solid from hazardous and/or contaminating contact with the ambient during transport.

5   **BRIEF DESCRIPTION OF THE DRAWINGS**

A more complete understanding of the invention may be obtained by reference to the drawings, in which:

FIG. 1 depicts a flow diagram of a basic embodiment of a synchronously modulated flow-draw ("SMFD") ALD system in accordance with the invention;

10   FIG. 2 depicts in schematic form a comparison between prior art ALD process, SMFD-ALD process, and pulse and hold SMFD-ALD process;

FIG. 3 depicts schematically a perimeter slot valve at the close position in accordance with the invention;

FIG. 4 depicts schematically a perimeter slot valve at the open position in 15 accordance with the invention;

FIG. 5 depicts schematically a gap-controlling perimeter slot valve at the close position in accordance with the invention;

FIG. 6 depicts schematically a gap-controlling perimeter slot valve at the open position in accordance with the invention;

20   FIG. 7 highlights the seal area of a gap-controlling perimeter slot valve showing the seal purge line;

FIG. 8 depicts schematically a semi-perimeter slot valve at the close position in accordance with the invention;

FIG. 9 highlights in schematic form a design for inflatable seal element 25 shown deflated in accordance with the invention;

FIG. 10 highlights in schematic form a design for inflatable seal element shown inflated in accordance with the invention;

FIG. 11 illustrates the inflatable seal assembly (with reference to FIG. 10) in accordance with the invention;

30   FIG. 12 illustrates the inflatable seal assembly (with reference to FIG. 10) showing the inflation gas line and the connection with the inflatable seal in

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accordance with the invention;

FIG. 13 depicts the same inset as in FIG. 12 where the seal is shown inflated in accordance with the invention;

FIG. 14 depicts a perimeter slot valve seal area showing an elastomer diaphragm for gap control in the deflated state in accordance with the invention;

FIG. 15 depicts a perimeter slot valve seal area showing an elastomer diaphragm for gap control in the inflated state in accordance with the invention;

FIG. 16 depicts a perimeter slot valve seal area showing a metallic diaphragm assembly for gap control in the deflated state in accordance with the invention;

FIG. 17 depicts a perimeter slot valve seal area showing a metallic diaphragm assembly for gap control in the inflated state in accordance with the invention;

FIG. 18 depicts schematically a pressure-controlled source for gas and volatile liquid and solid precursors in accordance with the invention;

FIG. 19 depicts schematically a pressure-controlled source for non-volatile liquid precursors in accordance with the invention;

FIG. 20 depicts schematically a pressure-controlled source for non-volatile solid precursors in accordance with the invention; and

FIG. 21 depicts schematically a liquid delivery source in accordance with the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention is described herein with reference to FIGS. 1 – 21. For the sake of clarity, the same reference numerals are used in several figures to refer to similar or identical components. It should be understood that the structures and systems depicted in schematic form in FIGS. 1 – 21 serve explanatory purposes and are not precise depictions of actual structures and systems in accordance with the invention. Furthermore, the embodiments described herein are exemplary and are not intended to limit the scope of the invention, which is defined in the claims below.

FIG. 1 depicts a flow diagram of a basic embodiment of a synchronously

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modulated flow-draw ("SMFD") ALD system 600 in accordance with the invention described in US Patent Application No. 10/347575, PCT Application No. US03/01548, and the improvements that are disclosed in this application.

System 600 comprises a pressure-stabilized inert, purge-gas source 602 of
5   a purge gas 604. Purge gas is supplied through purge-source shut-off valve 102 and purge-source flow restriction element ("FRE") 103 into gas distribution chamber 104, which is commonly a conventional shower head. As depicted in FIG. 1, purge-source shut-off valve 102 and purge-source FRE 103 provide serial fluidic communication between purge-gas source 602 and gas distribution
10 chamber 104. In this specification, flow restriction elements (FREs) cause a pressure step-down when gas is flowing through them. A chemical reactant precursor in the form of a pure chemical gas, a vapor from a liquid or solid chemical, or mixtures of vapor or gas chemicals with inert gas is provided at well-controlled pressure at a plurality of chemical-gas sources 105, 105'. Chemical-gas
15 source 105 is connected in serial fluidic communication with booster chamber 107 through chemical-source-FRE 106. Booster chamber 107 is connected in serial fluidic communication with gas distribution chamber (showerhead) 104 through chemical-dosage shut-off valve 110 and booster-FRE 109. As depicted in FIG. 1, second chemical-gas source 105' is connected to showerhead 104 with devices
20 corresponding to those described with reference to chemical-gas source 105.

Gas-distribution FRE 113 provides serial fluidic communication between gas distribution chamber 104 and atomic layer deposition chamber ("deposition chamber") 114. In a preferred embodiment, in which gas distribution chamber 104 is a showerhead device, gas-distribution FRE 113 is commonly a nozzle array. A
25 nozzle array provides restricted and uniform flow from gas distribution chamber 104 to deposition chamber 114, which contains a substrate being treated. A substrate supporting chuck with means to control the substrate temperature, 620, is disposed within deposition chamber 114.

Deposition chamber 114 is connected in serial fluidic communication to a
30 small-volume draw-gas introduction chamber ("DGIC") 630 through deposition-chamber FRE 115. Inert draw-gas source 602 is connected in serial fluidic

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communication to DGIC 630 through draw-gas line 119, draw-source shut-off valve 120, and draw-source-FRE 121. Draw-gas introduction chamber 630 is connected in serial fluidic communication through DGIC-FRE 632 to draw control chamber ("DC") 116. A chemical abatement element 634 is disposed inside DC 116. DC

5   116 is connected in serial fluidic communication to pump chamber 636 through draw-control outlet 124 and draw-control FRE 117. A pressure gauge 638 is connected to DC 116. Pressure gauge 638, for example, an MKS Baratron model 628 type, monitors the process through, for example, the average pressure in DC 116. Similarly, other process monitoring devices (not shown), such as gas

10   analyzers, can be conveniently connected to DC 116. Low pressure gauge 644, such as an HPS I-Mag cold-cathode gauge, is attached to pump chamber 636 to monitor chamber pressure during idle time. Turbomolecular pump 640 is connected to pump chamber 636 through a pumping gate-valve 642 to facilitate high vacuum during idle time and high-throughput flow during ALD operation. For

15   example, a pump selected from the BOC-Edwards STPA series is suitable. Good performance for ALD deposition on 200 mm silicon wafers was obtained using an STPA 1303C pump. Turbomolecular pump 640 is evacuated using backing pump 642. For example, a BOC QDP40 or equivalent serves well as backing pump 642. In other embodiments in accordance with the invention, higher pumping-speed

20   pump arrangements, such as the QMB series from BOC Edwards, facilitate remote location placement of dry pumps, as known in the art.

In certain preferred embodiments, reactive gas is added to DC 116 to enhance chemical abatement. Accordingly, system 600 comprises an ozone-supply manifold. Oxygen or oxygen-nitrogen mixtures are supplied from gas

25   cylinder 650. A mass flow controller 652 controls the flow of gas into a commercially available ozone generator 654. For example, the MKS Astex AX8407 series ozone generators perform well in SMFD system 600. The output from ozone generator 654 is monitored by ozone monitor 656, allowing feedback-control stabilization of ozone concentrations. Pressure controller 658, for example,

30   an MKS 640A type, maintains a selected constant pressure inside ozone generator 654. For the purpose of pulsing ozone into DC 116 while maintaining controlled

flow and pressure that are necessary for correct operation of ozone generator 654,
an ozone reservoir 660 comprises a volume selected to suppress the impact of
ozone pulsing on the pressure inside ozone generator 654. This allows pulsing of
reactive ozone into DC 116, while maintaining a desired flow and pressure in

5   ozone generator 654. Pressure controller 662 controls the pressure in ozone
reservoir 660. Ozone degradation is minimized in system manifold 600 by
maintaining the ozone supply manifold at substantially room temperature and by
minimizing the stagnant volume between ozone generator 654 and DC 116. For
example, the stagnant volume is described schematically in FIG. 1 by the dead-leg

10   between valve 664 and junction 668. Ozone is fed to ozone shut-off valve 664 and
ozone-source FRE 666 through the inner tubing of a double-wall line and fed to the
inlet of pressure controller 662 by the return flow between the inner and the outer
tubing. In this manner, the impact of ozone depletion in the stagnant space is
minimized by reducing the dead-leg between valve 664 and junction 668 to less

15   than 1 cc. Preferably, an ozone-eliminating catalytic converter 670 is disposed at
the outlet of pump 642 to suppress ozone emission to the ambient.

In a preferred embodiment, the functionality of chemical-dosage shut-off
valves 110, 110' was integrated into a multiple-port chemical introduction valve
comprising both 110 and 110'. Electrically actuated valves with response time in

20   the millisecond and submillisecond range are most suitable as actuators. Fast
pneumatic valves with millisecond response time also were utilized successfully
and also are adequate.

During typical ALD operation, apparatus 600 is switched essentially
between two static modes, a purge mode and a chemical-dosage mode.

25   Representative valve-settings of the two basic modes of operation are presented in
Table 1.

TABLE 1

Mode	Valve 102	Valve 120	Valve 110
Purge	OPEN	CLOSED	CLOSED
Chemical dosage	CLOSED	OPEN	OPEN

For clarity, the method for operating the SMFD system is described for the

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case of steady pressure process. As explained in the previous section, this mode commonly produces good results for critical applications. Also, as described above, it is understood that an ALD process typically comprises a cycle having at least four distinct stages, and the cycle is repeated multiple times in sequence to

5   deposit the desired thin film. The two modes described with reference to Table 1 and FIG. 1 are representative for a chemical-dosage stage and a purge stage of a typical four-stage cycle. In purge mode, for known purge-source pressure of purge-gas source 602, FREs 103 and 113 are designed to deliver a desired flow, Q_{purge}, of purge gas from purge-gas source 602 into gas distribution chamber 104,

10   and from there through gas distribution chamber 104, deposition chamber 114, DGIC 630, and DC 116 into draw-control outlet 124, and maintain showerhead pressure P_{purge}^{SH} and ALD deposition-chamber P_{114} at purge mode. In chemical dose mode, for known pressure of chemical-gas source 105, FRE 106 and 109 are designed to deliver chemical reactant gas to gas distribution chamber

15   (showerhead) 104 typically at a chemical-dosage flow rate, Q_{CD}, which is preferably substantially less than Q_{purge}. This lower flow is accompanied by lower showerhead pressure, P_{CD}^{SH}. Because the pressures in deposition chamber 114 and gas distribution chamber 104, P_{114} and P_{104}, respectively, are much lower (typically measured in mTorr) than the pressure of chemical-gas source 105

20   (typically measured in units of Torr), FREs 106, 109 are typically designed so that chemical-dosage flow rate, Q_{CD}, is practically independent of pressures P_{114} and P_{104}. In chemical-dosage mode, draw-gas source 602 at known draw-gas-source pressure supplies draw gas at a desired draw-gas flow rate to DGIC 630 through FRE 121. In accordance with the invention, the draw-gas-source pressure at

25   source 602 and FRE 121 determine the draw-gas flow rate through DGIC 630. This draw-gas flow rate and FRE 632 establish chemical-dosage draw pressure in DGIC 630. The draw pressure increases as draw-gas flow rate increases. The difference in pressure between deposition chamber 114 and DGIC 630, together with the conductance of FRE 115, determines the draw of process gas, including

30   unreacted chemical precursor, out of deposition chamber 114. The draw of unreacted chemical precursor from deposition chamber 114 into and through DGIC

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630 and into DC 116 also contributes slightly to the total flow rate of gases through DGIC 630, and therefore to the draw pressure. An increase in the chemical-dosage draw pressure in DGIC 630 reduces the draw from deposition chamber 114 into and through DGIC 630 and DC 116. Conversely, a decrease in the

5   chemical-dosage draw pressure in DGIC 630 increases the draw from deposition chamber 114. Preferably, dose steps are designed for maximized chemical flux and minimized usage of chemicals. For an extreme example, a typical 300 cc to 400 cc ALD chamber for the processing of 200 mm wafers will be practically free of chemical depletion effect at chemical dose pressures from 200 mTorr.

10   Accordingly, implementing a dose of 100% chemical at 200 mTorr typically requires negligible additional flow of dose chemical beyond the effect of the booster. Indeed, we have empirically found that the impact of additional dose beyond the booster dose of trimethylaluminum ("TMA") used for ALD of Al_2O_3 at 300°C was less than 2% under dose conditions of undiluted precursor at 200

15   mTorr. Accordingly, implementation of typical <10 sccm of TMA steady-state flow was sufficient to achieve optimized ALD performance.

In preferred embodiments in accordance with the invention described in US Patent Application No. 10/347575, PCT Application No. US03/01548, and the improvements described herein, in addition to the two static modes, that is, a

20   purge mode and a steady-state chemical dosage mode, a significant transient mode is designed into the initiation of chemical dosage. An initial transient flow rate is generated by chemical-gas flow from booster chamber 107. Given time to equilibrate when valve 110 is closed, the pressure in booster chamber 107 is equal to the pressure at chemical-gas source 105, $P_{107}^{static} = P_{105}$. When valve 110 is open

25   under steady-state conditions, the steady-state pressure at 107, P_{107}^{SS}, is smaller than P_{105} due to the pressure gradient over FRE 106. When shut-off valve 110 is actuated to open, the initial pressure at booster chamber 107 transients from P_{105} down to the steady-state pressure, P_{107}^{SS}. The flow of chemical reactant gas into gas distribution chamber 104 during chemical dosage is determined by the

30   pressure at booster chamber 107 and the conductance of FRE 109. A pressure transient at booster chamber 107 causes a pressure transient at gas distribution

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chamber 104. As a result, during the pressure transient in booster chamber 107, the corresponding flow of chemically reactive gas into deposition chamber 114 conforms to an initial pulse that gradually decreases to the steady-state flow rate. Concurrently, the draw pressure in DGIC 630 conforms to an initial pulse that

5 transients upwards. The transient time is determined mainly by the volume of DC 116, the draw flow rate, and the conductance of FRE 117. During the pressure transient in 116, the draw out of deposition chamber 114 follows a downward transient. Selective design of the conductance of each of FREs 106, 109, and 117, and the draw flow of the volumes of booster chamber 107 and DC 116 is

10 used to match transient flow and transient draw to minimize pressure-excursions in deposition chamber 114. It is an important aspect of the invention described in US Patent Application No. 10/347575, PCT Application No. US03/01548, and the improvements described in this invention, however, that pressure excursions are internally suppressed by an SMFD system (especially when operated at steady

15 pressure) even when transient-time constants are not perfectly matched and various valve actuations are not perfectly synchronized. In fact, a major advantage of SMFD implementation as taught in some of the embodiments of the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548 is the convenient and cost-effective insensitivity of performance to

20 apparatus and process imperfections.

Steady-state flow rates during a chemical-dosage stage are typically 1/10 to 1/100 of the purge-gas flow rate during a purge stage. The time scale to establish a steady state of chemical dose is therefore unacceptably long. To avoid this throughput penalty, effective chemical dose steps, according to embodiments of

25 the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548, are tailored to provide an initial fast flow of chemical at the initial stage of chemical dose steps. Accordingly, the initial flow transient serves to reduce significantly the response time of a chemical-dosage stage. This reduced response time is important for enhancing the efficiency and throughput of

30 an ALD process. During the initial transient part of a chemical dosage stage, the volumes of gas distribution chamber 104 and deposition chamber 114 are quickly

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filled by a pulse of chemical-gas at an initially high pressure and at a corresponding initially high transient flow rate. Initial transient flow rate during chemical dosage is typically adjusted to match the purge flow rate of inert purge gas flow during a preceding purge stage. Accordingly, continuity of flow is

5   preserved. Gas distribution chamber 104 and deposition chamber 114 are quickly filled with chemical gas because the residence time of chemical gas flowing through the chambers is short, corresponding to the initially high chemical-dosage flow rate. Booster chamber volume and booster FREs are selectively designed to substantially match the draw chamber pressure increase at the initial stage of

10 chemical dose. Booster chamber volume is also designed to provide an integrated booster exposure on the order of 1 pressure×volume to 2 pressure×volume equivalents. For example, if the deposition chamber volume is 400 cc and the dose pressure is 200 mTorr, the booster volume is designed to provide a booster exposure of 0.08 liter×Torr to 0.16 liter×Torr. When ALD system 600 is switched

15 from a chemical-dosage mode to a purge mode, the transients are usually much less important. The relatively small volume of gas distribution chamber 104 is quickly loaded to P_{purge}^{SH} through the relatively high conductance of FRE 103. If small volume draw control chambers are implemented, pressure drop in DC 116 from a chemical-dosage draw pressure to a purge-draw pressure is much faster

20 than purge residence time, and the switching from dose to purge can occur on a timescale of several msec. If, however, as explained before, the volume of the draw chamber is large, the response time for draw control chamber pressure drop is longer than the purge residence time in the process chamber. For example, under a typical process used for ALD on 200 mm wafers, the residence time in the

25 process chamber is 3 msec. Draw pressure modulation between chemical dose and purge are on the order of 10% to 20% of the total draw pressure. Typically, draw chamber volume of 1 liter to 5 liters is convenient for integrating abatement capability into the system. Accordingly, the draw chamber pressure modulation follows a typical time constant of 10 msec to 20 msec. As a result, some process

30 chamber excursions are unavoidable at the end of a dose step. However, as expected, these pressure modulations resulted in no measurable performance

penalty. Likewise, there is no reason to intentionally produce a transient, such as in the case of the initial pulse of a chemical-dosage stage. Accordingly, transient effects associated with terminating a chemical-dosage stage are insignificant.

5 As described above, an SMFD ALD system in accordance with the invention described in US Patent Application No. 10/347575 and PCT Application No. US03/01548 resolves the conventional trade-off between the need for high flow (and low pressure) during purge (to enable efficient and short-time purge) and the need for low flow (and high pressure) during chemical dose (to enable fast reaction and high chemical utilization). In a steady-pressure embodiment, the

10 system is able to maintain substantially constant process pressure while the flow rates are modulated by more than a factor of ten. In fact, we have successfully implemented process hardware and recipes with flow modulations exceeding a factor of 100. Alternatively, both pressure and flow can be modulated in order to gain even higher efficiencies for purge and chemical-dosage stages with virtually

15 no trade-off effects. An apparatus and a method in accordance with the invention achieve this desired capability by modulating the draw (flow of gas out of the deposition chamber) in synchronization with modulating the flow of gas into the deposition chamber.

FIG. 2 presents a schematic comparison between prior art flow versus time

20 chart 300 and the inlet flow into an SMFD showerhead 104, chart 320. Since typical SMFD timing is more than 5 times shorter, the time scale of the SMFD charts is divided by a factor of 5. Chart 340 represents the complementary flow versus time into the DGIC 630 in synchronization with the inlet flow depicted in chart 320. An ALD cycle comprised of first chemical dose 302, first purge 304,

25 second chemical dose 306, and second purge 308 is conventionally carried under substantially constant flow conditions as illustrated in chart 300. In contrast, the inlet sequence 320 of first chemical dose 322, first purge 324, second chemical dose 326, and second purge 328 is carried under substantially modulated flow conditions. Complementary draw flow presented in chart 340 maintains the

30 pressure during chemical dose steps with draw flow 342 and 344 during chemical dose steps 322 and 326, respectively. Note the transient stages 321 and 325 at

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the leading edge of chemical dose 322 and 326, respectively.

A further improvement in chemical utilization splits the chemical dose steps into pulse and hold in accordance with Table 2.

TABLE 2

Mode	Valve 102	Valve 120	Valve 110
Purge	OPEN	CLOSED	CLOSED
Chemical dose **PULSE**	CLOSED	OPEN	OPEN
Chemical dose **HOLD**	CLOSED	OPEN	CLOSED

5

The flow versus time is illustrated in chart 360. Accordingly, the first chemical dose includes transient 361, low flow steady-state 362, and no flow period 363. Similarly, the second chemical dose includes transient 365, low flow steady-state 366, and no flow 367. When valve 110 shuts off during the dose, the

10 flow into the deposition chamber ceases. The deposition chamber becomes a dead-leg and the pressure in deposition chamber 114 transients down slightly to match the pressure in DGIC 630. If chemical depletion is not prominent, dose time is extended at no additional increase in chemical utilization. This improved mode of chemical dose can be utilized to improve the quality of ALD films by extending

15 chemical reaction time to facilitate further completion of these reactions. The global rate of the typically first order ALD reactions is proportional to the flux of chemicals and concentration of unreacted sites. Naturally, as the reaction propagates, the number of reactive sites decreases and accordingly the global reaction rate decreases. In many ALD processes, the inevitable residual

20 concentration of reactive sites that is not reacted at the end of the chemical dose step contributes to the inclusion of impurities in the film. In particular, embedded OH groups are detrimental to insulating properties of dielectric ALD films. Therefore, in some ALD processes, film quality may require extended chemical dose exposures. The pulse and hold mode given in Table 2 and illustrated in chart

25 360 advantageously extends the actual dose exposure while avoiding the penalty of increasing chemical utilization. For example, TMA dose of 50 msec was utilized with only 10 msec to 20 msec of pulse and complementary 30 msec to 40 msec of hold on our SMFD system. The pulse and hold mode further improves chemical utilization efficiencies by eliminating any pressure gradients in deposition chamber

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114 during the HOLD time. This decoupling between the exposure (flux multiplied by dose time) and the utilization of chemical is a key advantage of pulse and hold SMFD.

The pulse and hold mode enables efficient chemical utilization during low temperature ALD. ALD reactions are thermally activated. At low temperatures, ALD reactions are slow and inefficient. To minimize dose times, ALD precursors are dosed at maximized pressure and 100% concentration. Pulse and hold SMFD mode is advantageously implemented to suppress the loss of chemical during dose. A pulse and hold sequence was implemented for TMA dose during SMFD-ALD of Al_2O_3 at 100°C. A fully saturated process step required only 20 msec of pulse and 30 msec of dose (total of 50 msec dose time). Material utilization was still greater than 5%, which is extremely good for such low temperature process that was executed with such short dose time.

A useful range for dose was attempted successfully between 5 msec to 120 msec, and a useful range of hold was tested from a minimum of 5 msec up to 200 msec. Preferably, dose is carried with a 5 msec to 50 msec duration, and hold is carried with a 20 msec to 100 msec duration. Mostly a preferred range of 5 msec to 25 msec for dose and 15 msec to 35 msec for hold is recommended.

The term "chamber" and related terms refer to a component having a relatively substantially enclosed volume, V, with at least one inlet and one outlet, in which within a range of useful flow rates, Q, the pressure gradient, ΔP, across the chamber (e.g., between an inlet and an outlet) is substantially smaller than the average pressure, P, in the chamber. Generally, in embodiments in accordance with the invention, the ratio $\Delta P/P$ of a chamber is less than 0.1 when V is about 1000 cc and the flow, Q, through the chamber is about 1000 sccm or less. Also, in this specification, a gas has a substantial residence time inside a chamber, for which residence time is defined by $\tau = VP/Q$. Generally, in the specification, the residence time, τ, in a chamber is typically 50 μsec or longer.

In contrast, the term "flow restricting element" ("FRE") refers to a component having a negligible volume and typically having only one inlet and one outlet, in which within the range of useful flow rates, Q, the pressure gradient, ΔP, is

relatively large compared to the average pressure, P, between the inlet and the outlet of the FRE. Generally, in a FRE in this specification, the ratio $\Delta P/P$ is greater than 0.1 when the flow, Q, through the FRE is about 1000 sccm or less. Also, in this specification, the residence time, τ, of a gas in a FRE is relatively short, generally, less than 50 μsec.

Much like an electrical circuit that has basic passive elements such as resistors, capacitors, and inductors, chambers with $\Delta P = 0$ (non-FRE character) and FREs with V = 0 do not practically exist. Nevertheless, in an analogy to electrical circuit conventions, ALD and other fluid-flow networks containing chambers and FREs can be practically explained and designed by assigning pure component properties to basic elements.

Therefore, one skilled in the art understands the description and design of flow systems using idealized properties of chambers and FREs. For example, the term "process chamber" means that in the process space, pressure gradients are generally minimized, although it is clear that pressure gradients exist wherever there is flow in a flow system. Indeed, in certain embodiments of SMFD in accordance with the invention, an elongated process chamber is designed to include a pressure gradient across it.

FREs are typically designed and idealized to have zero or minimum volume, although it is known to those skilled in the art that there is no practical way to implement FREs with V = 0. It is also understood that, unless specifically stated, processes are advantageously practiced in chambers in which ΔP is negligible. On the other hand, in some instances, a FRE having negligible V (or τ) is not practical. Yet, a FRE with a significant volume is commonly used with no performance penalty. The properties of a FRE having a significant volume is practically described and designed by combining a pure chamber, V, and a pure FRE, much like the electrical description of electrical circuit elements, for example, inductors with resistance, that are described by an "equivalent circuit".

Accounting for the volume of a FRE can be included in designs by increasing a proximate chamber's "effective" volume. Accounting for the flow-restricting property of a chamber can be achieved by adding the residual

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conductance of the chamber to the conductance of a downstream FRE to obtain

an "effective FRE" conductance, C_{eff}, whereby $C_{eff} = \dfrac{1}{\dfrac{1}{C_{FRE}} + \dfrac{1}{C_{chamber}}}$.

Systems that practically have several FREs in series and parallel may be represented by effective FREs to simplify description of the systems. For example,

5   a line that contains a capillary and a valve, both being FREs, may be represented by a single effective FRE. In preferred embodiments in accordance with the invention described in US Patent Application No. 10/347575, PCT Application No. US03/01548, and the improvements described herein, flow-resistance properties are designed into the construction of valves.

10   The challenge of efficient ALD comes from the contradictory requirements for efficient purge and efficient chemical dosage. Neither of these important modes can be seriously compromised in achieving overall efficiency and practically low maintenance. Chemical dosage stages should be made as short as possible, with maximized precursor flux. The higher the concentration and flux of chemical,

15   the shorter the dosage step. Also, parasitic sources of residual chemicals are handled better by a higher flux of majority chemical being dosed. Many ALD precursors have relatively low vapor pressures, making the delivery of high chemical flow rates difficult. In this respect, embodiments in accordance with the invention described in US Patent Application No. 10/347575, PCT Application No.

20   US03/01548, and the improvement of this invention enhance the ability to deliver undiluted chemical.

FIGS. 3 and 4 depict in schematic form a cross-section of a preferred ALD reactor vessel 800. As shown in FIG. 3, reactor vessel 800 comprises a reactor-vessel wall 802, a reactor-vessel top 804, and a vessel-bottom 806, which define a

25   vessel interior 808. Reactor vessel 800 includes gas distribution chamber (showerhead) 201. A showerhead inlet 809 at top 804 serves as an inlet for chemical reactant gases and purge gases into showerhead 201. Nozzle array (FRE) 202 separates the bottom of gas distribution chamber 201 from ALD deposition chamber (process chamber) 203. A substrate 204 is supported on

30   heated wafer chuck (substrate holder) 205, made from a thermally conducting

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metal (e.g., W, Mo, Al, Ni) or other materials commonly used in the art for hot susceptors and chucks. Wafer chuck 205 includes a wafer lift-pin mechanism 810. Wafer transport is accomplished with aid of lift pins 812 (only one out of three pins shown), as known in the art. Wafer lift pins 812 are actuated to lift wafer substrate

5   204 above the top surface of chuck 205 using actuator 814 and levitation arm 816. Deposition chamber 203 is confined by deposition-chamber FRE 206. A draw-gas introduction chamber ("DGIC") 820 is located downstream from deposition chamber 203, between FRE 206 and DGIC-FRE 822. A draw control chamber ("DC") 208 is located downstream from DGIC, and is confined by DGIC-FRE 822

10 and draw-control FRE baffle 209. Chemical-abatement element 824 is disposed inside DC 208. Spacer 826 provides direct thermal contact of chemical-abatement element 824 and draw-control FRE baffle 209 with heated wafer chuck 205.

Draw-gas inlet 830 provides serial fluidic communication between a draw-gas manifold (not shown) and a draw gas plenum 832. One skilled in the art can

15 implement draw gas plenum 832 in many different configurations, and the embodiment shown in FIGS. 3 and 4 is a non-exclusive example. As depicted in FIG. 3, draw-gas inlet 830 is in fluidic communication with radial plenum space 832, which further communicates with DGIC 820 through a radial array of nozzles (not shown), which are appropriately spaced and designed to unify the radial flow

20 distribution of gas into DGIC 820 and direct draw gas into the upstream portion of DGIC 820. Those who are skilled in the art can appreciate the necessity to adequately unify the flow of draw gas and reactive abatement gas to conform to the symmetry of the deposition system. For example, the radial symmetry of the system is depicted in FIGS 3 and 4. Indeed, a draw control gas, introduced with a

25 substantially non-uniform radial distribution, impacted the radial distribution of dosed chemicals as observed when ALD was tested with one of the dose steps kept under saturation conditions. While saturation properties of ALD reaction steps can overcome this effect, longer chemical doses are dictated that, in turn, extend the ALD cycle time.

30   Optionally, reactive gas is delivered from a reactive gas manifold (not shown) through line 840 into reactive-gas plenum 842. Reactive-gas plenum 842

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serves to shape a uniform radial flow distribution of reactive abatement gas into draw chamber 208. For example, the reactive gas is delivered into a radial channel that communicates with draw chamber 208 through a plurality of horizontal nozzles that are appropriately spaced and designed. One skilled in the

5   art can appreciate that reactive gas plenum system 842 can be implemented in many different configurations in accordance with the invention.

During ALD processing, purge gas during a purge stage and chemical reactant gas during a dosage stage flow along a process-gas flow-path through reactor-vessel interior 808 in a downstream direction from showerhead inlet 809

10   through showerhead 201, deposition chamber 203, DGIC 820, and DC 208, in that order, and out of reactor vessel 800 through vacuum port 210. Similarly, draw gas introduced into DGIC 820 flows in a downstream direction from DGIC 820 into DC 208 and then exits through vacuum port 210. The terms "downstream" and "upstream" are used herein in their usual sense. It is a feature of embodiments in

15   accordance with the invention that backflow of gases, that is, the flow of gases in an "upstream" direction, never occurs, as explained above. The term "upstream" is used in this specification, however, to designate the relative locations of components and parts of a system.

Reactor vessel 800 further includes a perimeter slot valve ("PSV") 850. As

20   depicted in FIGS. 3 and 4, PSV 850 comprises a substrate-transport slot 852 through reactor-vessel wall 802, a continuous perimeter cavity 854 (FIG. 4) within reactor-vessel wall 802, a continuous sealing poppet 856, and an actuator 858 for moving sealing poppet 856 between an open position (FIG. 4) and a closed position (FIG. 3). Sealing poppet 856 is moved into perimeter cavity 854 in the

25   closed position (FIG. 3), and sealing poppet 856 is moved out of perimeter cavity 854 in the open position (FIG. 4). Substrate-transport slot 852 is substantially coplanar with the substrate-supporting surface of substrate holder 205. Perimeter cavity 854 is substantially coplanar with substrate-transport slot 852. Substrate-transport slot 852 defines a substrate-transport channel through reactor-vessel

30   wall 802 to substrate holder 205 when sealing poppet 856 is in open position (FIG. 4), and sealing poppet 856 separates substrate-transport slot 852 from vessel

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interior 808 when sealing poppet 856 is in its closed position (FIG. 3).

Reactor-vessel wall 802 defines a vessel perimeter within the reactor-vessel wall, and sealing poppet 856 conforms to the vessel perimeter when sealing poppet 856 is in its closed position (FIG. 3). As depicted in FIGS. 3 and 4, reactor-

5   vessel wall 802 comprises a substantially radially symmetric shape, and sealing poppet 856 comprises a substantially radially symmetric shape. It is understood that other embodiments of reactor vessel 800 and PSV 850 in accordance with the invention could have other geometric shapes. As depicted in FIG. 3, sealing poppet 856 in its closed position forms an inner sealing wall 862 of the process-

10   gas flow-path in vessel interior 808. Inner sealing wall 862 comprises a radially symmetrical shape, which promotes a radially symmetric flow of gasses along the process-gas flow-path and, thereby, enhances uniform deposition and reduces formation of solid deposits. In the particular embodiment of reactor vessel 800 as depicted in FIG. 3, a portion of inner sealing wall 862 defines a portion of DGIC

15   820. As depicted in FIG. 4, PSV 850 comprises a fixed upper sealing surface 870, an upper poppet sealing surface 872 corresponding to fixed upper sealing surface 870, an upper peripheral seal 873, a fixed lower sealing surface 874, a lower poppet sealing surface 876 corresponding to fixed lower sealing surface 874, and a lower peripheral seal 877. Upper sealing surfaces 870, 872, lower sealing

20   surfaces 874, 876, and peripheral seals 873, 877 are configured to seal the vessel interior when sealing poppet 856 is in its closed position (FIG. 3).

As depicted in FIG. 4, upper peripheral seal 873 and lower peripheral seal 877 are assembled on poppet sealing surfaces 872, 876, respectively. Also, seals 873, 877 are configured as o-ring seals. It is clear that different types of seals, for

25   example, flat gasket seals, are useful, and that seals 873, 877 can be assembled on fixed sealing surfaces 870, 874, instead of on poppet sealing surfaces 872, 876. Suitable materials for seals 873, 877 include elastomer materials made from Viton, Kalrez, Chemraz, or equivalents. One skilled in the art is capable of implementing perimeter slot valve 850 in many different configurations.

30   Substrate-transport slot 852 and the associated wafer transport system communicated through slot 852 are completely isolated from the ALD process

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system in reactor vessel interior 808 when PSV 850 is closed.

The implementation of the preferred embodiment has revealed that the high flow of inert gas into the leading edge of the DFIC during chemical dose was sufficient to provide exceptional protection against possible film buildup in radial

5   crevices 882 and 884 that are formed between 804 and 856 and between 856 and 802, respectively. Accordingly, PSV was implemented with no adverse impact on maintenance cycle or performance.

The PSV can be further utilized to reduce the conductance of FRE 115 between process chamber 114 and DGIC 630 (FIG. 1). Smaller 115 conductance

10   increases the pressure gradient between process chamber 114 and DGIC 630 with several fold advantages. First, a better suppression of backflow is established. Second, at any given flow, the pressure gradient across process chamber 114 is reduced. Finally, the DGIC is better defined and the requirements for draw flow radial uniformity are relaxed. However, in the embodiment of FIGS. 3 and 4, the

15   range for narrowing the gap between 804 and 205 which defines the conductance of FRE 115 is limited by the need to provide a convenient path for wafer transport. However, in the embodiment presented in FIGS. 5 and 6, the constraint of the wafer-loading path is removed with the implementation of a gap-controlling PSV. As illustrated in FIG. 5, the gap-controlling PSV implements a convex lower

20   surface 880 on the bottom of a wider poppet 856' to narrow the gap 206 between 880 and chuck 205. The resulting conductance of gap 206 can be as low as necessary since, as shown in FIG. 6, when the PSV is opened to facilitate wafer transport, gap-controlling surface 880 is raised and therefore does not interfere with the transport path. Gap-shaping portion 880 of PSV poppet 856' is preferably

25   shaped with a down-looking substantially convex smooth continuation of part 804 to minimize flow disturbance.

To facilitate the gap-controlling PSV, the inner sealing gaskets and gasket grooves 872' and 873' are relocated as illustrated in FIG. 6. Likewise, top sealing surface 870' is relocated.

30   In the PSV embodiment displayed in FIG. 3, crevices 882 and 884 next to sealing gaskets are effectively shielded from the ALD precursors by the high flow

of inert gas in the DGIC. However, in the gap-controlling PSV embodiment (FIG. 5), the gap of the inner seal is located inside process chamber 114 and therefore is no longer protected. Accordingly, entrapment of ALD precursors can adversely impact the memory of the ALD chamber and can lead to fast deterioration of the

5 inner seal if growth of inferior films in the gap is not suppressed. To overcome this problem, the gap must be purged with a slow flow of inert gas during chemical dose. FIG. 7 illustrates schematically the seal area of the PSV. Only the right side of a cross-sectional view is shown. Gap 882 between poppet 856' and top 804' is purged through a delivery line 886 that is machined into the body of part 804'.

10 In another embodiment illustrated in FIG. 8, the inner seal of the PSV is completely eliminated and poppet 856" forms a solid assembly with top part 804". Bellow 888 allows the entire assembly to elevate when the PSV is moved to the OPEN position. In this case, purge gas connection line 612 and the connections of chemical sources 105 and 105' (FIG. 1) are made flexible to accommodate an ~12

15 mm of vertical motion. Accordingly, flexible hoses, bellows, or high purity Teflon line sections are implemented.

Another embodiment that is well-suited to eliminate the pitfalls of crevice 882 associated with the inner PSV seals is presented in FIGS. 9, 10, 11, 12, and 13. In this embodiment, crevice 882 is protected by an inflated elastomer seal.

20 The elastomer seal is made, for example, from suitable materials such as Viton, Kalrez, Chemraz, or equivalent and is mounted inside ledge 890 located under seal surface 870". When the PSV is at the upper position (PSV OPEN), elastomer 892 is not inflated as shown in FIG. 9. When the PSV is at the lower position (PSV SHUT), elastomer 892 is inflated by applying inert gas or air pressure through

25 conduit 894. As a result, inflated elastomer 892 creates a seal against an appropriately shaped surface on poppet 856'''. For example, FIG. 9 depicts a concave shaped portion 889 of 856''' that accommodates the curved shape of inflated seal 892. Following this inflation, crevice 882 is eliminated and only a small portion 896 of inflated seal 892 is exposed to the process (FIGS. 10 and 13).

30 In one preferred embodiment of this invention, the inflated seal is made from a slightly permeable elastomer. Inflation with inert gas results in a slow flow of inert

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gas through the elastomer at exposed area 896. Accordingly, this inert gas flow suppresses the growth of films on exposed area 896 during process. In another alternative embodiment, the elastomer is appropriately perforated at the 896 area to provide a path for inert gas flow and protection to area 896 from process

5   chemicals.

Inflated elastomer seal 892 can be implemented in many different designs according to this invention. For example, FIGS. 11 and 12 illustrate a specific preferred design. Part 804" is split into an inner portion 898 and an outer portion 900. Appropriately-shaped elastomer seal 892 is folded and pressed between 898

10   and 900 and sealed into a substantially triangular-shaped tube by the pressure of upper and lower sealing ledges 902 and 904, respectively (FIG. 11). Inflation path 906 is machined into one or both of inner and outer parts 898 and 900 as depicted in FIG. 12. Against that path, elastomer 892 is appropriately shaped to conform around a metallic ferrule 908. The pressure of sealing ledges 910 and 912 seals

15   the elastomer over ferrule 908 and in communication with inflation channel 906. Accordingly, an inflation/deflation path 914 is created. FIG. 13 displays a larger view of seal 892 after inflation.

In another preferred embodiment, this invention implements standard PSV design such as the design that is described above in reference to FIGS. 3 and 4.

20   The conductance of FRE 115 between process chamber 114 and DGIC 630 (FIG. 1) is controlled with a flexible diaphragm. In particular, two different designs are given here for better clarity.

In the first embodiment illustrated in FIGS. 14 and 15, a flexible elastomer-made diaphragm 920 seals over radial cavity 922. For the sake of simple

25   illustration, only the right corner of a radial symmetry system is shown in the cross-sectional view. Cavity 922 is connected through line 924 to a pressurized source of air or inert gas. As illustrated in FIG. 15, when cavity 922 is pressurized, diaphragm 922 flexes down to effectively create a convex surface and to narrow gap 206' down. The pressure in cavity 922 can be controlled to affect the

30   stretching and deflection of diaphragm 920 and, effectively, the dimension of gap 206'. Diaphragm 920 is preferably made from Viton, Kalrez, Chemraz, or

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equivalent. In some embodiments, diaphragm 920 is made from slightly permeable elastomer and cavity 922 is pressurized with inert gas. Accordingly, slow flow of inert gas that emerges from the surface of diaphragm 920 serves to suppress undesired growth of film on the surface of the diaphragm. Alternatively,

5 diaphragm 920 is perforated to facilitate the flow of inert gas when the diaphragm is pressurized. Accordingly, the conductance of FRE 115 can be reduced and adjusted for best process results when PSV 850 is down. During wafer transport, the diaphragm is de-pressurized by evacuation (FIG. 14) to clear the path for the wafer and the end-effector.

10 In another embodiment, diaphragm 926 is made from a metallic alloy such as Algiloy or Nimonic. The diaphragm is pre-shaped in accordance with conventional art. A tension spring 928 is connected to the inner side of diaphragm 926 substantially at the center of the diaphragm and to the inner top surface of cavity 922. When cavity 922 is not pressurized, the tension force applied by spring

15 928 pulls diaphragm 926 back and the downward side of the diaphragm is concave. Practically, spring 928 is implemented with multiple tension springs evenly spaced around inside the annular shaped inflation chamber 922. As illustrated in FIG. 17, when cavity 922 is pressurized, diaphragm 926 is pushed down and overcomes the force of spring 928. If the pressure is high enough,

20 diaphragm 926 is converted to have a downward convex shape. As a result, the conductance of FRE 115 can be substantially reduced by making gap 206" smaller. This ability to alternate the conductance of FRE 115 between two substantially different values allows better SMFD performance without sacrificing wafer transport compatibility. Accordingly, the conductance of FRE 115 (gap 206")

25 can be reduced for best process results when PSV 850 is down. During wafer transport, the diaphragm is de-pressurized (FIG. 16) to clear the path for the wafer and the end-effector.

SMFD advantageously lends itself to a simple chemical source design. In particular, the ability of SMFD to dose vaporized liquid and solid chemicals without

30 a carrier gas is compatible with a simplified pressure-controlled chamber source where the vapor pressure of the chemical can be accurately controlled as

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described in the exemplary embodiments below. Accordingly, the difficulties to control the partial pressure from chemical precursors in the flow of carrier gas as described in the introduction is circumvented. SMFD source is depicted in FIGS. 18, 19, and 20. Source chamber volume is chosen to improve pressure-stability

5 and to compensate for the slow response of the pressure control device or method. Accordingly, it is advantageous to ensure that source chamber capacity (i.e., in liter×Torr) is substantially larger than the material delivered per cycle. For example, source capacity that is 20 times to 100 times larger than the capacity loss per dose lends itself to a minimized pressure ripple in the source chamber,

10 i.e., 316 in FIG. 18, within 1% to 5%, which is tested to have indistinguishable impact on the consistency and length of the chemical dose. Pressure control devices cannot follow the speed of SMFD dose cycles. Rather, these devices will be set to control the average pressure in the source chamber. Therefore, the volume of the source is chosen to limit pressure fluctuation, as necessary.

15 Three different pressure control methods are described in FIGS. 18, 19, and 20. In FIG. 18, a relatively high vapor pressure from liquid or solid chemical 306 is controlled by a commercially available pressure controller 312 such as the MKS Instruments 640A series which is limited to operation temperature in the range from 0°C to 50°C. The chemical is located at a separate container 302 and is

20 heated or cooled per temperature control element 304 to provide a pressure, P_{chem}, that is larger than the pressure that is needed in source 316. This pressure is fed into the inlet of pressure controller 312 that controls the pressure inside source chamber 316. A shut-off valve 308 is placed between chemical container 302 and pressure controller 312 to terminate chemical supply through conduit 310 when

25 processing is complete. Correct choice of appropriate pressure controller and chemical temperature ensures stable and consistent chemical delivery. In particular, the choice of pressure controller conductance must be suitable for the necessary flow under given pressure conditions as known in the art and described, for example, in the user manual of the 640A pressure controllers from MKS

30 Instruments. The temperature of source 300, including gas line 310 interconnecting the chemical container with the pressure controller, pressure

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controller 312, the gas line 314 interconnecting the pressure controller and source chamber 316, and gas line 318 interconnecting the source chamber with the SMFD-ALD manifold at source points 105 and 105' (FIG. 1) must be maintained at a temperature adequately high to prevent condensation of the precursor

5   chemicals, as known in the art. Source evacuation is accomplished through utility valve 320, conduit 322, and vacuum pump 324.

In another embodiment depicted in FIG. 19, consistent and controlled pressure from relatively non-volatile liquid chemicals is achieved by applying liquid delivery techniques to deliver the precursor with precision into a vaporizing

10   chamber. Vaporization chamber 406 is connected to source chamber 402 through heated gas line 408. The pressure is monitored at the source chamber using a conventional pressure gauge such as the model 628 or the model 631 Baratron manufactured by MKS Instruments, which are suitable to reliably measure the pressure of chemicals and can be maintained at temperatures of 100°C and

15   200°C, respectively, to prevent condensation of non-volatile chemicals. Vaporized precursor is delivered to chemical source point 105 through conduit 412. The entire assembly downstream from vaporizer 406 is controlled at a temperature suitable to prevent condensation of the chemical. In certain embodiments, the temperature of vaporizer 406 is controlled separately and independently to

20   improve vaporization efficiency, speed, and control. Valve 416 is utilized to evacuate the source chamber through conduit 418 and vacuum pump 420.

Liquid delivery control system 400 does not need to accommodate the ALD dose response, but rather to be able to sustain a consistent delivery over a longer time scale. However, as stated in the introduction, most commercially available

25   liquid delivery systems are not suitable to deliver such small quantities as required for ALD practice that are in the order of 10^{-4} cc/cycle. In the case of SMFD with ~2 cycles/sec, the liquid delivery system must be able to precisely control flow on the order of 0.012 cc/min. This minute chemical flow is in the low range of, for example, top-of-the-line DLI-25C system manufactured by MKS Instruments (low

30   limit of 0.006 cc/min). In addition, to maintain the volume of the source chamber conveniently small, the liquid delivery system must accommodate a relatively fast

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start/stop operation, preferably on the order of a cycle time which is difficult to achieve with commercially available technology. An embodiment that accomplishes consistent delivery of small liquid flow with fast response is described with respect to the schematic illustration given in FIG. 21.

5   Liquid delivery system 450 implements container 454 that is filled with liquid precursor 452 from chemical line 472 through inlet valve 470. Line 472 is connected to a liquid filling line (not shown) that draws liquid precursor from a chemical reservoir such as the EpiFill system from Epichem, Inc. A variable air chamber 456 completes the makeup of container 454 with a flexible bellow 458.

10   The liquid can be pressurized by introducing air from pneumatic line 464 through valve 462 into air chamber 456 to force chamber 456 to expand downwards and pressurize the liquid. The liquid can be depressurized by evacuating the pressurized air out of chamber 456 through valve 466 into line 468. Accordingly, the liquid can be pressurized and depressurized within 5 msec to 50 msec with

15   standard solenoid valves. Variable orifice 460, for example, a proportional valve, is used to control the flow of liquid towards outlet 410. When metallic bellow 458 approaches, maximum extension container 454 is automatically refilled. For example, bellow 458 approaches the bottom of container 454 where a magnetic proximity sensor is mounted. A magnet inside chamber 456 is sensed at proximity

20   and the system will refill container 454 within the next idle time. The proximity sensor is designed to sense the need for refill when system 450 is still capable of delivering enough chemical for an entire interval between idle times. Alternatively, two liquid delivery systems 450 may be connected to a single source 400 and alternately serve and refill. Refilling is accomplished by depressurizing chamber

25   456 and pushing liquid through valve 470 to retract bellow 458 and refill container 454.

As noted in the introduction, solid chemicals present several source design challenges. In particular, the inconsistency of evaporation rate from solid chemicals due to fluctuation in the area of the solid material makes seeding vapors

30   from solid source into carrier gas expensive and unreliable. An embodiment for a vapor source from solid chemical is described here with reference to FIG. 20.

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Source chamber 526 is connected to source point 105" (equivalent to 105 and 105' in FIG. 1) through an appropriately heated conduit (not shown). The volume of source chamber 526 is chosen to reduce pressure fluctuations as described above. Source chamber 526 is connected to vaporizer 512 through conduit 522.

5   Vaporizer 512 is further connected to sublimation chamber 501. Solid source assembly 500 is sectioned into three thermal zones. The first thermal zone, 502, includes sublimation chamber 501. The second thermal zone, 510, includes vaporizer 512. The third thermal zone, 520, includes conduit 522, source chamber 526, pressure gauge 528, utility valve 524, and point source 105". The

10   temperature of second zone 510 is controlled to maintain the desired source pressure. Third zone 520 is maintained at a temperature higher than the temperature of second zone 510 to prevent solid material condensation in source chamber 526, pressure gauge 528, utility valve 524, and source point 105". For example, the temperature of third zone 520 is maintained at 10°C to 20°C higher

15   than the temperature of second zone 510. The temperature of first zone 502 is typically held at a temperature equal to or higher than the temperature of second zone 510. Thermal barrier 506 is located between zone 502 and zone 510, and thermal barrier 516 is located between zone 510 and zone 520 to ensure accurate and independent temperature control at each zone and to minimize temperature

20   gradients across the zones as practiced in the art of thermal and mechanical design.

Source assembly 500 is further connected via utility valve 524 to chemical fill point 530 and through conduit 532 and valve 533 to vacuum pump 534. Precursor loading is accomplished through utility valve 524 when the system is

25   idle. The solid material is preferably introduced as a thoroughly mixed slurry of fine powder solid chemical with an inert, highly volatile liquid such as freon, carbon tetrachloride (CCl$_4$), trichloroethylene, or Galden HT55 from Solvag Solexis, to name a few alternatives. The liquid is used to shield the precursor from ambient exposure during transfer since most precursors react violently with moisture and/or

30   oxygen. A slurry is better suited than a solvent since it is more generic. In addition, solvated precursor can still react with the ambient while wet, and

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immersed solid particles in a slurry are practically isolated from contact with the ambient. Utility valve 524 is preferably located with a line of sight straight above sublimation chamber 501. The slurry is poured into sublimation chamber 501 and preferably flushed with a small portion of the slurry liquid to remove the solid

5   powder particles from vaporizer 512 and utility valve 524 and flush them down into sublimation chamber 501. In another embodiment (not shown), utility valve 524 is connected directly to sublimation chamber 501. This embodiment, however, requires that utility valve 524 is maintained within temperature zone 502, which disadvantageously limits the temperature range of zone 502 to the maximum

10   temperature that can be tolerated by the valve.

Following chemical delivery, the slurry is located in sublimation chamber 501. The source assembly is evacuated through utility valve 524, conduit 532, and valve 533 into vacuum pump 534 to effectively pump out any trace of ambient air and evaporate the liquid from the slurry. The elevated temperature maintained in

15   source assembly 500 ensures complete removal of the slurry liquid within a short evacuation time. Following the evacuation, the temperature of zone 502 is elevated to effectively and quickly sublime all the powder 504 from sublimation chamber 501. Vaporizer 512 is designed with high surface area and appropriate conductance to effectively condense the solid material on the area of vaporizer

20   512 and prevent the high pressure vapors from reaching conduit 522. The condensed solid covers the surface of 512 with a layer 514 of solid. Pressure is maintained by the equilibrium between solid 514 and vapor and, at steady state, is determined solely by the temperature of zone 510. Vaporization rate from solid 514 scales with the area. Accordingly, at any given desired operation temperature,

25   vaporizer area is selected to ensure that vaporization rate can adequately compete with the rate that chemical is being drawn out of source 526 during dose. For ALD purposes, the volume of source chamber 526 serves to smooth pressure fluctuation during actual dose and, therefore, the rate of vaporization need only be capable of replenishing the pressure during the entire cycle. Accordingly,

30   equilibrium pressure is maintained with virtually no pressure drop during process. Preferably, adequate area for vaporizer 512 is designed excessively to ensure

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stable source operation. As an example, the embodiment depicted in FIG. 20 implements vaporizer 512 with a multiple stack of high purity nickel tubing (shown in schematic cross-sectional view). However, many different designs and materials can be used as long as care is taken to ensure that, during sublimation

5 of solid 504 and condensation of solid 514, the path through vaporizer 512 is not significantly being clogged. The capacity of vaporizer 512 to solid chemical 514 increases as the design becomes more open. However, open design may render the vaporizer practically too large. To maintain vaporizer 512 at smaller sizes, source 500 may be operated with several cycles of sublimation and usage.

10 The temperature of zone 510 is feedback-controlled to maintain the desired pressure monitored by gauge 528. When solid 514 starts to deplete, some of the area of vaporizer 512 becomes bare of solid chemical. Pressure differential between set pressure and the actual pressure increases, and eventually the temperature of zone 510 sharply increases to mark the transition from an

15 equilibrium source into a sublimation source. Both pressure fluctuations (the "error" on the feedback-controlled loop) and temperature rise predict that the source must be replenished. The pressure fluctuations are a very sensitive gauge to indicate source exhaustion and need for refill far ahead of adverse impact on the ALD process performance. The difficulty to maintain pressure with a sublimation

20 source is eliminated by the vaporizer scheme that, given an appropriately sized vaporizer 512 area, is able to circumvent the inconsistency of sublimation source. With appropriately chosen source chamber 526 volume, the pressure fluctuations are set as low as needed and below the level that impacts performance. Finally, end-point detection and practical and efficient chemical loading method are also

25 advantageous. Accordingly, source 500 eliminates all the known problems of solid sources and is fully compatible with SMFD.

To remove the solid chemical, sublimation chamber 501 is maintained at low temperature by cooling down zone 502. The solid condenses at chamber 501. When all of the remaining solid chemical is transferred to chamber 501, the

30 pressure drops at pressure gauge 528. Inert liquid is introduced through utility valve 524 to cover solid 504. Subsequently, source 500 is vented and sublimation

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chamber 501 is disconnected from vaporizer 512. The liquid protects chemical 504 from ambient exposure. Similarly, following the procedure of collecting the chemical within the sublimation chamber and immersion in inert liquid, pressure gauge 528, and/or utility valve 524 or the entire source assembly 500 can be

5 removed for maintenance, replacement, or repair.

Systems, apparatuses, and methods designed and operated in accordance with the invention are particularly useful in ALD technology. Synchronous modulation of flow and draw, SMFD, is also useful, however, in a wide variety of circumstances and applications. It is evident that those skilled in the art may now

10 make numerous uses and modifications of the specific embodiments described, without departing from the inventive concepts. It is also evident that the steps recited may, in some instances, be performed in a different order; or equivalent structures and processes may be substituted for the structures and processes described. Since certain changes may be made in the above systems and

15 methods without departing from the scope of the invention, it is intended that all subject matter contained in the above description or shown in the accompanying drawings be interpreted as illustrative and not in a limiting sense. Consequently, the invention is to be construed as embracing each and every novel feature and novel combination of features present in or inherently possessed by the systems,

20 devices, and methods described in the claims below and by their equivalents.

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CLAIMS

1.   A method of conducting atomic layer deposition, comprising:

conducting a chemical dose stage, said chemical dose stage comprising flowing a chemical reactant gas to substantially fill up a deposition chamber;

5   substantially reducing said flow of said chemical reactant gas while concurrently reducing the flow out of the deposition chamber by increasing the pressure downstream to the deposition chamber to substantially match said flow out of said deposition chamber to said chemical reactant gas flow into said deposition chamber;

10   terminating the flow of said chemical into said deposition chamber while concurrently substantially matching the pressure downstream from said deposition chamber to the pressure in said deposition chamber to substantially suppress said flow out of said deposition chamber; and

continuing said chemical dose stage for a specified time without further 15   introduction of chemical flow.

2.   A method as in claim 1 wherein said pressure downstream to the deposition chamber is increased by flowing gas into a draw gas introduction chamber (DGIC) located in serial fluidic communication downstream from said deposition chamber.

20   3.   A method as in claim 1 wherein said conducting atomic layer deposition comprising conducting SMFD-ALD.

4.   An ALD system comprising:

a perimeter slot valve (PSV) in a reactor vessel;

said PSV comprising:

25   a substrate-transport slot through said reactor-vessel wall;

a continuous perimeter cavity within said reactor-vessel wall;

a continuous sealing poppet; and

an actuator for moving said sealing poppet between an open position and a closed position;

30   wherein said sealing poppet is moved into said perimeter cavity in said closed position, said sealing poppet is moved out of said perimeter cavity in said

open position, said substrate-transport slot is substantially coplanar with a substrate-supporting surface of said substrate holder, said perimeter cavity is substantially coplanar with said substrate-transport slot, said substrate-transport slot defines a substrate-transport channel through said reactor-vessel wall to said

5 substrate holder when said sealing poppet is in said open position, and said sealing poppet separates said substrate-transport slot from said vessel interior when said sealing poppet is in said closed position;

wherein said PSV comprises:

a fixed upper sealing surface;

10 an upper poppet sealing surface corresponding to said fixed upper sealing surface;

an upper peripheral seal;

a fixed lower sealing surface;

a lower poppet sealing surface corresponding to said fixed lower

15 sealing surface; and

a lower peripheral seal;

wherein said upper sealing surfaces, said lower sealing surfaces, and said peripheral seals are configured to seal said vessel interior when said sealing poppet is in said closed position;

20 wherein said substrate holder is larger than said substrate;

wherein the perimeter area of said substrate holder is not covered by the substrate;

wherein said sealing poppet creates a substantially radial narrow gap between said uncovered perimeter area of said substrate holder and the bottom

25 surface of said poppet when said PSV is in said closed position;

wherein said radial narrow gap is narrower than said substrate transport slot when said PSV is in said closed position; and

said radial narrow gap is wider than said substrate transport slot when said PSV is in said open position.

30 5.   A system as in claim 4 wherein said ALD comprising conducting SMFD-ALD.

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6.   A PSV as in claim 4 wherein said bottom surface of said poppet is designed with a substantially down-looking convex shape.

7.   A PSV as in claim 4 wherein a purge gas is introduced at substantially low flow between said fixed upper sealing surface and said upper

5   poppet sealing surface.

8.   A PSV as in claim 4 wherein:

a radial inflatable seal is formed between said fixed upper sealing surface and said upper poppet sealing surface;

the seal is inflated when said PSV is closed; and

10   the gap downstream from said upper peripheral seal between said fixed upper sealing surface and said upper poppet sealing surface is substantially filled with said inflatable seal when said inflatable seal is inflated.

9.   The PSV as in claim 8 wherein:

said inflatable seal is made from a slightly permeable polymer and said

15   inflatable seal is inflated with high purity inert gas; and

the area of said inflated seal that is located between said fixed upper sealing surface and said upper poppet sealing surface and is exposed to the process is substantially purged by the flow of said high purity inert gas out of said inflated seal.

20   10.   The PSV as in claim 8 wherein:

said inflatable seal is made from a perforated polymer and said inflatable seal is inflated with high purity inert gas; and

the area of said inflated seal that is located between said fixed upper sealing surface and said upper poppet sealing surface and is exposed to the

25   process is substantially purged by the flow of said inert gas out of said inflated seal.

11.   An ALD system comprising:

a semi-perimeter slot valve (SPSV) in a reactor vessel, said SPSV comprising:

30   a substrate-transport slot through said reactor-vessel wall;

a continuous perimeter cavity within said reactor-vessel wall;

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a continuous sealing poppet; and

an actuator for moving said sealing poppet between an open position and a closed position;

wherein said sealing poppet is moved into said perimeter cavity in said

5   closed position, said sealing poppet is moved out of said perimeter cavity in said open position, said substrate-transport slot is substantially coplanar with a substrate-supporting surface of said substrate holder, said perimeter cavity is substantially coplanar with said substrate-transport slot, said substrate-transport slot defines a substrate-transport channel through said reactor-vessel wall to said

10   substrate holder when said sealing poppet is in said open position, and said sealing poppet separates said substrate-transport slot from said vessel interior when said sealing poppet is in said closed position;

wherein said SPSV comprises:

a chamber top;

15   a flexible metal bellow seal allowing said chamber top to move up and down while maintaining vacuum seal;

a fixed lower sealing surface;

a lower poppet sealing surface corresponding to said fixed lower sealing surface; and

20   a lower peripheral seal;

wherein said lower sealing surfaces and said peripheral seal are configured to seal said vessel interior when said sealing poppet is in said closed position;

wherein said substrate holder is larger than said substrate;

wherein the perimeter area of said substrate holder is not covered by the

25   substrate;

wherein said sealing poppet creates a substantially radial narrow gap between said uncovered perimeter area of said substrate holder and the bottom surface of said poppet;

said radial narrow gap is narrower than said substrate transport slot when

30   said SPSV is in said closed position; and

said radial narrow gap is wider than said substrate transport slot when said

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SPSV is in said open position

12. An SPSV as in claim 11 wherein said chamber top includes a gas distribution showerhead and said ALD comprising SMFD-ALD.

13. An SPSV as in claim 11 wherein an ALD manifold is mounted on said
5 chamber top and connected to gas and chemical sources with flexible hose means.

14. An SMFD-ALD apparatus wherein the conductance between a process chamber and a draw gas introduction chamber is reduced by means of an inflatable diaphragm;
10   said inflatable diaphragm is located above the perimeter area of the substrate holder;

wherein said perimeter area of the substrate holder is not covered by the substrate during process;

a radial-ring shaped diaphragm is located substantially above said
15 perimeter area of said substrate holder;

the conductance out of said process chamber is substantially defined by the gap between said ring-shaped diaphragm and said perimeter area of substrate holder;

said gap is narrowed down when said diaphragm is inflated;
20   said diaphragm is inflated by pressurizing a substantially small inflation chamber located above said diaphragm; and

said small inflation chamber is sealed from said process chamber by said diaphragm.

15. The apparatus as in claim 14 wherein said diaphragm is made from
25 an elastomer material.

16. The apparatus as in claim 15 wherein said elastomer material is slightly permeable and said diaphragm is inflated with pure inert gas; and

when said diaphragm is inflated, a slow flow of said inert gas emerges from said diaphragm into said process chamber to effectively purge the area of said
30 diaphragm and protect said diaphragm from the process.

17. The apparatus as in claim 15 wherein said elastomer material is

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perforated and said diaphragm is inflated with pure inert gas; and

when said diaphragm is inflated, a slow flow of said inert gas emerges from said diaphragm through said perforation into said process chamber to effectively purge the area of said diaphragm and protect said diaphragm from the process.

5   18.   The apparatus as in claim 14 wherein said diaphragm is made from a metallic alloy and said diaphragm is pulled into said inflation chamber with a tension spring;

said diaphragm is maintained in a down-looking concave position by the tension of said spring when said diaphragm is not inflated; and

10   said diaphragm is inverted from a down-looking concave surface into a down-looking convex surface when the diaphragm is inflated.

19.   A chemical vapor source for SMFD-ALD apparatus comprising:

a chemical container;

a pressure controller in serial fluidic communication downstream from said

15   chemical container; and

a source chamber in serial fluidic communication downstream from said pressure controller;

wherein a set pressure of said chemical vapor is maintained in said source chamber by said pressure controller.

20   20.   The chemical source as in claim 19 wherein the capacity of said source chamber exceeds the capacity loss per ALD cycle by a factor of 10.

21.   The chemical source as in claim 19 wherein the capacity of said source chamber exceeds the capacity loss per ALD cycle by a factor of 100.

22.   A chemical vapor source for SMFD-ALD apparatus comprising:

25   a liquid delivery system;

a vaporizer in serial fluidic communication downstream from said liquid delivery system; and

a source chamber in serial fluidic communication downstream from said vaporizer;

30   wherein a set pressure of said chemical vapor is maintained in said source chamber by controlling the liquid delivery into said vaporizer; and

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said controlling controls said liquid delivery to maintain said set pressure.

23. The chemical source as in claim 22 wherein the capacity of said source chamber exceeds the capacity loss per ALD cycle by a factor of 10.

24. The chemical source as in claim 22 wherein the capacity of said source chamber exceeds the capacity loss per ALD cycle by a factor of 100.

25. A liquid delivery system wherein a controlled flow of liquid through a proportional valve is driven by an expandable pressure chamber;

the expansion of said expandable pressure chamber protrudes into a liquid filled chamber;

wherein said pressure chamber is separated from said liquid filled chamber with an expandable flexible metallic bellow; and

said pressure chamber is inflated to expand the bellow into said liquid filled chamber to effectively pressurize the liquid and trigger the flow.

26. A pressure controlled chemical source wherein a sublimation chamber is connected in serial fluidic communication with a vaporizer and the vaporizer is connected in serial fluidic communication with a source chamber and the source chamber is connected in serial fluidic communication to an SMFD-ALD manifold;

wherein said sublimation chamber is loaded with solid chemical;

said chemical is sublimed from said sublimation chamber to condense on the wall area of said vaporizer;

a desired vapor pressure of said solid chemical is maintained in said vaporizer and said source chamber corresponding to the vapor pressure of said chemical at the temperature of said vaporizer;

wherein said wall area of vaporizer is substantially high to substantially maintain the desired vapor pressure when the chemical is being utilized for SMFD-ALD process;

wherein the conductance of said vaporizer from said sublimation chamber into said source chamber and the temperature of said sublimation chamber during sublimation of said solid chemical out of said sublimation chamber and for condensation onto said wall area of said vaporizer provides for effective

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condensation of substantially all of said solid chemical over said vaporizer wall area; and

buildup of said solid chemical over the wall area of said source chamber is substantially prevented.

5   27.   The chemical source as in claim 26 wherein said solid chemical is loaded into said sublimation chamber with a slurry of fine powder and inert liquid;

wherein the liquid has a low boiling temperature;

said inert liquid does not substantially dissolute said solid chemical; and

said inert liquid is vacuum evaporated away from said chemical source to

10   effectively leave a pure and dry solid chemical inside the sublimation chamber.

28.   A method to enhance the safety of solid chemical delivery into and out of a chemical source by immersing the solid material in a substantially non-solvating inert liquid with low boiling temperature to effectively protect said reactive solid from hazardous and/or contaminating contact with the ambient during

15   transport.

29.   The chemical source as in claim 26 implemented for general delivery of chemical from solid into a CVD process chamber.

30.   An SMFD-ALD apparatus with improved SMFD performance implementing low conductance between process chamber and DGIC.

20   31.   The chemical source as in claim 26 wherein the capacity of said source chamber exceeds the capacity loss per ALD cycle by a factor of 10.

32.   The chemical source as in claim 26 wherein the capacity of said source chamber exceeds the capacity loss per ALD cycle by a factor of 100.

33.   An ALD apparatus and method capable of dosing chemicals with

25   source vapor pressure lower than 1 Torr within less than 100 milliseconds.

34.   An ALD apparatus and method capable of dosing chemicals with source vapor pressure lower than 0.5 Torr within less than 200 milliseconds.

35.   A method of performing atomic layer deposition (ALD) comprising:

flowing a pulse of deposition gas into a deposition chamber, said pulse

30   lasting for a time less than 200 milliseconds;

holding said deposition gas in said deposition chamber for a time less than

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200 milliseconds without additional gas flow into said chamber; and

purging said deposition gas from said chamber.

36.   A method as in claim 35 wherein said pulse length is between 1 msec and 50 msec and said hold time is between 10 msec and 100 msec.

5   37.   An atomic layer deposition system comprising:

a deposition chamber;

a gas draw chamber;

a flow restriction element located between said deposition chamber and said gas draw chamber; and

10   a deposition chamber seal;

said deposition chamber, said gas draw chamber, said deposition chamber seal and said flow restriction element being concentric;

wherein a portion of said seal is located between said deposition chamber and said flow restriction element.

15   38. . An atomic layer deposition system comprising: ..

a deposition chamber;

a gas draw chamber;

a deposition chamber seal having a seal gap area exposed to said deposition; and

20   a gas purge source connected to said seal gap.

39.   A method of atomic layer deposition comprising:

providing an atomic layer depositing apparatus having a deposition chamber and a deposition chamber seal gap, a portion of which seal gap is exposed to said deposition chamber;

25   depositing a thin film in said deposition chamber; and

purging said seal gap portion exposed to said deposition chamber with purge gas during said depositing.

40.   An atomic layer deposition apparatus comprising:

a deposition chamber housing comprising a fixed housing portion and a

30   movable portion; and

said movable portion supported on a bellows.

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41.   An atomic layer deposition apparatus comprising;

a deposition chamber housing comprising a fixed housing portion and a movable portion;

a gap between said fixed housing portion and said movable portion; and

5   an inflatable seal for sealing said gap.

42.   An atomic layer deposition apparatus as in claim 41 wherein said seal is perforated and further including a source of purge gas connected to said gap.

43.   An atomic layer deposition apparatus as in claim 41 and further including a shaped seat against which said seal seats when inflated.

10

44.   An atomic layer deposition apparatus as in claim 41 and further including a ferrule located interior to said inflatable seal.

45.   An atomic layer deposition apparatus comprising;

a deposition chamber housing comprising a fixed housing portion and a movable portion;

15

a gap between said fixed housing portion and said movable portion;

a movable diaphragm for sealing said gap; and

a source of pressurized gas for controlling the position of said diaphragm.

46.   An atomic layer deposition apparatus as in claim 45 wherein said apparatus comprises a deposition chamber within said housing and a gas draw chamber and wherein said movable diaphragm controls a flow restriction element between said deposition chamber and said gas draw chamber.

20

47.   An atomic layer deposition apparatus as in claim 45 wherein said diaphragm is made of a metallic alloy.

25

48.   An atomic layer deposition apparatus as in claim 45 and further including a spring attached to said diaphragm for controlling the position of said diaphragm.

49.   A chemical vapor source for an atomic layer deposition apparatus, said source comprising:

30

a sublimation material container;

a container heat source;

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a vapor exit port connected to said container; and

a sublimation surface exposed to said sublimation container, said sublimation surface having an area of at least twice the surface area available for material in said container.

5 50.   A chemical vapor source as in claim 49 wherein said sublimation surface is located between said container and said vapor exit port.

51.   A chemical vapor source as in claim 49 wherein said sublimation surface is located above said container, said source further including a slurry entry port located above said sublimation surface.

10 52.   A thin film deposition system comprising:

a thin film deposition chamber;

a vaporizer communicating with said deposition chamber; and

a liquid source communicating with said vaporizer;

said liquid source comprising:

15 a liquid reservoir having a reservoir volume sufficient to hold enough liquid for a complete deposition process; and

an expandable pressure chamber communicating with said liquid reservoir, said expandable pressure chamber having an expandable volume; and

20 wherein said expandable volume of said expandable pressure chamber is at least 25% of said reservoir volume.

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FIG. 1

Prior Art Inlet Flow

SMFD Inlet Flow

SMFD DC Flow

SMFD Pulse and Hold mode

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

858

882

886

804'

856'

FIG. 7

FIG. 8

858

894

889

870"

890

892

856'''

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

FIG. 16

FIG. 17

FIG. 18

FIG. 19

FIG. 20

FIG. 21